U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-283 401

Washington State Refineries: Petroleum, Petroleum Derivatives and Wastewater Effluent Characteristics

Oceanographic Inst of Washington, Seattle

Prepared for

National Oceanic and Atmospheric Administration, Seattle, Wash

Mar 78

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-78-040	2.	3. RECIPIENT'S ACCESSION NO. PB283401
4. TITLE AND SUBTITLE Washington State Refineries: Petroleum, Petroleum Derivatives and Wastewater Effluent Characteristics		5. REPORT DATE March 1978 issuing date
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Pizzo, Joseph T., Harshman, Gary W., Johnson, Thomas L.		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Oceanographic Institute of Washington Washington State Commerce Building 312 First Avenue North Seattle, WA 98109		10. PROGRAM ELEMENT NO. EHE 625-A
		11. CONTRACT/GRANT NO. 03-6-022-35189 (NOAA)
12. SPONSORING AGENCY NAME AND ADDRESS Office of Energy, Minerals, & Industry Office of Research & Development U.S. Environmental Protection Agency Washington, D.C. 20460		13. TYPE OF REPORT AND PERIOD COVERED final report (May-Nov 1976)
		14. SPONSORING AGENCY CODE EPA/600/17

15. SUPPLEMENTARY NOTES

This project is part of the EPA-planned and coordinated Federal Interagency Energy/Environment R&D Program. (P.O.: C. Hall, 8-426-4567, Headquarters)

16. ABSTRACT

This report presents the results of a study of wastewater effluent characteristics of refineries in Washington State, compiled for NOAA as part of an Environmental Assessment of Northern PugetSound and the Strait of Juan de Fuca. The purpose of the study was to describe in detail the types of petroleum and petroleum derivatives that potentially could reach the waters of Puget Sound. This was achieved through the collection and summary of available information on the chemical characteristics, amounts processed, and final disposition of crude oils, refined products, and wastewater effluents associated with the six Puget Sound refineries.

Sources for this information included the literature, federal and state government agencies, the petroleum industry, and academic institutions. The report describes the amounts and types of petroleum and its derivatives handled by Puget Sound refineries and the amounts typically reaching marine waters. Further, the refining and waste treatment processes employed by the area refineries are described in detail.

17. (Circle One or More) KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS			b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Ecology	Hydrology, Limnology	Energy Conversion	[illegible]	~~6F~~ ~~8A~~ ~~8F~~
[✓ Environments]	Biochemistry	Physical Chemistry		~~8H~~ ~~10A~~ ~~10B~~
Earth Atmosphere	Earth Hydrosphere	[✓ Materials Handling]		~~7B~~ ~~7C~~ ~~13B~~
Environmental Engineering	Combustion	Inorganic Chemistry		
Geography	[✓ Refining]	Organic Chemistry		
		Chemical Engineering		
Other:				

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 186
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE PC E06 MF A01

DOC United States
Department of
Commerce

National Oceanic and Atmospheric Administration
Environmental Research Laboratories
Seattle, Washington 98115

EPA United States
Environmental Protection
Agency

Office of Energy, Minerals and Industry
Office of Research and Development
Washington, D.C. 20460

EPA-600 7-78-040
March 1978

PB 283 401

WASHINGTON STATE REFINERIES: PETROLEUM, PETROLEUM DERIVATIVES, AND WASTEWATER EFFLUENT CHARACTERISTICS

Interagency
Energy-Environment
Research and Development
Program Report

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EPA-600/7-78-040
March 1978

WASHINGTON STATE REFINERIES: PETROLEUM, PETROLEUM DERIVATIVES AND WASTEWATER EFFLUENT CHARACTERISTICS

by

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Prepared for the MESA (Marine Ecosystems Analysis) Puget Sound Project, Seattle, Washington in partial fulfillment of

EPA Interagency Agreement No. D6-E693-EN
Program Element No. EHE625-A

EPA Project Officer: Clinton W. Hall (EPA/Washington, D.C.)
NOAA Project Officer: Howard S. Harris (NOAA/Seattle, WA)

This study was conducted
as part of the Federal
Interagency Energy/Environment
Research and Development Program

Prepared for

OFFICE OF ENERGY, MINERALS, AND INDUSTRY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

November 1976

UNITED STATES DEPARTMENT OF COMMERCE
Juanita M. Kreps, Secretary

NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
Richard A. Frank, Administrator

Environmental Research Laboratories
Wilmot N. Hess, Director

Completion Report Submitted to
PUGET SOUND ENERGY-RELATED RESEARCH PROJECT
MARINE ECOSYSTEMS ANALYSIS PROGRAM
ENVIRONMENTAL RESEARCH LABORATORIES

by

OCEANOGRAPHIC INSTITUTE OF WASHINGTON
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ACKNOWLEDGEMENTS

The contributions of the following individuals and organizations is gratefully acknowledged. Their help in answering questions and providing access to much needed information on the oil refining industry has helped ensure production of a comprehensive and reputable report on wastewater effluent characteristics of the refineries in Washington State.

ACADEMIA

William Brewer, Institute for Environmental Studies, University of Washington, Seattle, Washington

Robert Stokes, Institute for Marine Studies, University of Washington, Seattle, Washington

STATE

Richard Burkhalter, Department of Ecology, Olympia, Washington

Edward Miller, Washington State Energy Office, Olympia, Washington

FEDERAL

Robert C. Clark, Jr., Research Oceanographer, National Marine Fisheries Service (NOAA), Seattle, Washington

James Sweeney, Water Compliance and Permits Department, Environmental Protection Agency, Seattle, Washington

Nick Malueg, Surveillance and Analysis Division, Environmental Protection Agency, Seattle, Washington

H.D. Van Cleave, Chief, Spill Prevention and Control Branch, Environmental Protection Agency, Washington, D.C.

Robert Hackman, Federal Energy Administration, Seattle, Washington

Craig L. Chase, Petroleum Regulation Branch, Federal Energy Administration, Seattle, Washington

John Adger, Energy Resource Development Division, Federal Energy Administration, Washington, D.C.

Don F. Guier, Division of Oil, Gas and Shale Technology, Energy Research and Development Administration, Washington, D.C.

Wade Watkins, Division of Oil, Gas, and Shale Technology, Energy Research and Development Administration, Washington, D.C.

Lieutenant (j.g.) Robert L. Skewes, Environmental Technology Branch, Office of Research and Development, U.S. Coast Guard, Washington, D.C.

Warren Waterman, U.S. Army, Corps of Engineers, Seattle, Washington

Leon Myers, Environmental Protection Agency Environmental Research Laboratory, Ada, Oklahoma

James Peterson, Data Analysis Division, Federal Energy Administration, Washington, D.C.

H.J. Coleman, Energy Research Center, Energy Research and Development Administration, Bartlesville, Oklahoma

Cathy Coronetz, Federal Energy Administration, Seattle, Washington

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I.I. Kamar, Manager, Olympic Pipe Line Company, Renton, Washington
D.T. Durrant, Coordinator, Planning and Economics, Trans Mountain Pipe Line Company Ltd., Vancouver, B.C., Canada
Alex Hunka, Trans Mountain Pipe Line Company Ltd., Vancouver, B.C. Canada
R.J. Young, Refining Associate, American Petroleum Institute, Washington, D.C.

In addition, consultant services on refinery technology and availability of data were provided by Waldemar Seton, P.E., of Seton, Johnson & Odell, Inc., Consulting Engineers, Portland, Oregon. Consultant review of the document was provided by Professor Lennart Johanson, Department of Chemical Engineering, University of Washington.

FINAL REPORT PREPARATION

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ABSTRACT

This report presents the results of a study of wastewater effluent characteristics of refineries in Washington State, compiled for the National Oceanic and Atmospheric Administration's (NOAA) Puget Sound Energy-Related Research Project. The purpose of this study was to describe in detail the types of petroleum and petroleum derivatives that potentially could reach the waters of Puget Sound. This was achieved through the collection and summary of available information on the chemical characteristics, amounts processed, and final disposition of crude oils, refined products, and wastewater effluents associated with the six Puget Sound refineries. Sources of this information included the literature, federal and state government agencies, the petroleum industry, and academic institutions. The following report describes the amounts and types of petroleum and its derivatives handled by Puget Sound refineries and the amounts typically reaching marine waters. Further, the refining and waste treatment processes employed by the area refineries are described in detail.

This study was performed under Contract No. 03-6-022-35189 with the National Oceanic and Atmospheric Administration (NOAA), administered through NOAA's Environmental Research Laboratories, Marine Ecosystems Analysis (MESA) Project Office, under an Interagency Agreement with the U.S. Environmental Protection Agency. The six-month study period extended from May 3rd through November 5th 1976.

I. INTRODUCTION

A. Purpose and Rationale

This document presents the results of a study of wastewater effluent characteristics of refineries in Washington State, compiled for the National Oceanic and Atmospheric Administration's (NOAA) Puget Sound Energy-Related Research Project. The purpose of this study is to place some perspective upon the types of petroleum and petroleum derivatives that potentially could reach the waters of Puget Sound. This was achieved through the collection and summary of available information on the chemical characteristics, amounts processed, and final disposition of crude oils, refined products, and wastewater effluents associated with the area refineries. Information and study data were collected from the literature, federal and state government agencies, the petroleum industry, and academic institutions. The following report describes the amounts and types of petroleum and its derivatives handled by Puget Sound refineries and the amounts typically reaching marine waters. Further, the refining and waste treatment processes employed by the area refineries are described in detail.

A description of the characteristics of crude oils and products transported in Puget Sound and the wastewater effluents released to the marine environment by the existing refineries is vital to the planning and design of a baseline investigation of petroleum and petroleum derivatives which may contaminate the waters of Puget Sound. The constituency and quality of effluents are dependent directly on the types of crudes processed, the refined products produced, refinery wastes incurred, and waste treatment processes used at each refinery. The study presents available data on the chemical constituents, process volumes, and characteristics of crude oils, refined products, and refinery wastes produced at Puget Sound refineries and imported into the state's marine waters.

The basic information assembled in this study (Work Unit B-3-1, described in Project Development Plan - Puget Sound Energy-Related Research Project, September, 1975) provides the necessary input for designing a water quality baseline study of petroleum hydrocarbon concentrations (Work Unit B-2-1). A combination of the outputs of Work Units B-3-1 and B-2-1 will help determine whether samples of refinery effluents adequately characterize the contamination existing in Washington waters or whether an analysis of refinery samples should be undertaken (Work Unit B-3-2). In addition, analysis of effluent characteristics that affect the biota in the area will help lay the foundation for future modeling efforts now being planned (Work Units D-2-3 through D-2-5).

As previously mentioned this refinery effluent study is a component of NOAA's Puget Sound Energy-Related Research (PSERR) Project. In addition, the identification and characterization of this data is useful to state planners and regulatory agencies.

B. Data Collection Procedure

The procedure of study consisted, essentially, of collecting, assembling and summarizing available information and data on the six refineries in Puget Sound. The following kinds of information were collected:

- Incoming Crude Oils: sources, volumes, chemical characteristics, pipeline versus marine transport.
- Refining Processes: general description of process units at each refinery.
- Refined Products Produced: product types, amounts, chemistry, and mode of product export.
- Wastewater Influent: general character and volumes of the different wastewater streams entering refinery treatment works.
- Wastewater Treatment Processes: general description of waste treatment processes used at each refinery and relative efficiencies of each process in treating specific wastewater constituents.
- Wastewater Effluent: characteristics and abundance of final wastewater effluent constituents.

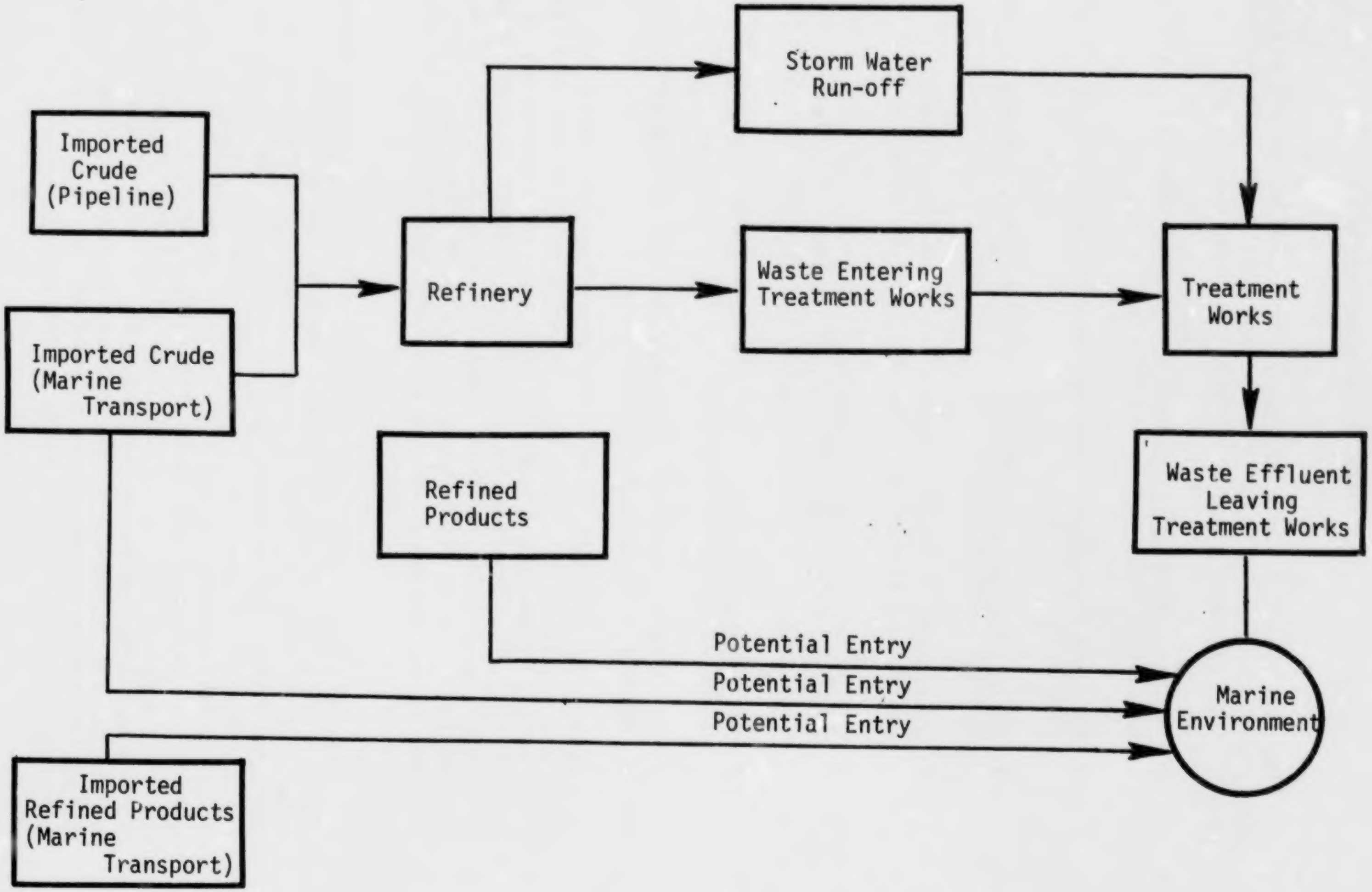
Figure 1 shows a process flow diagram that illustrates the kinds of information and data collected in this study.

Sources of information for this study included public and private agencies, firms and institutions. Data were gathered by in-person and telephone interviews with government and industry personnel and visitations to data-gathering agencies and data repositories in Washington State, Oregon, Oklahoma, and Washington, D. C. The refiners themselves were quite helpful by providing informative tours of the process and wastewater treatment units. Additional information was sought by the submittal of questionnaires directly to the oil refineries.

One particular problem in our data-collection efforts appeared early and persisted throughout the study. Most of the information currently available on refineries has been developed within the industry. Hence, all crude characteristics, for example, tend to stress the engineering and refining characteristics of the oils. Since the intent of this study is, in part, to identify constituents of petroleum and its derivatives that could potentially affect the quality of the marine environment, much of this information is not directly applicable. This problem was alleviated in certain parts of the study where some evaluation could be made of the relative toxicities of crude oil, refined product, and effluent parameters, based upon in-house interpretation of information contained in the literature. These data are presented in appropriate sections of the report.

Figure 1

Interrelationship of Data Types Collected and Processes Described


Imported Crude (Pipeline)
Imported Crude (Marine Transport)
Refinery
Storm Water Run-off
Waste Entering Treatment Works
Treatment Works
Waste Effluent Leaving Treatment Works
Refined Products
Imported Refined Products (Marine Transport)
Potential Entry
Potential Entry
Potential Entry
Marine Environment

Some information on the sources and types of crude oils used by each refinery was provided by the Federal Energy Administration (FEA), which has been formulating a national allocation plan for Canadian crude oil exports to U.S. refineries. Additional information on crude sources was provided by refineries themselves. Questionnaires, consisting of a list of needed information, were sent to refineries to gather this and other types of information. Figure 2 is a sample version of one of these questionnaires.

The questionnaire approach to data collection met with much success. Shell provided good, useable data on all requested information. The responses from Mobil, Atlantic Richfield Company (ARCO), Texaco, U.S. Oil and Refining and Sound Refining were less detailed, but provided useful information. Response time of the refineries was variable, ranging from one to three months.

Chemical characterizations of crude oils now utilized by Washington refineries, as well as potential future replacement crudes, were gathered from a variety of sources, including the literature, industry publications, (e.g., Oil & Gas Journal), and federal agencies. The key government repository for crude characterizations is the Energy Research and Development Administration's (ERDA) Energy Research Center in Bartlesville, Oklahoma (formerly with the Bureau of Mines), which routinely carries out chemical assays of foreign and domestic crude oils. During visits to the Washington, D. C., offices of the Environmental Protection Agency (EPA), ERDA, the American Petroleum Institute (API), and the Research and Development branch of the U.S. Coast Guard, interviews with key personnel emphasized that the Bartlesville facility is heavily relied upon as the major source of information on crude oil chemistry by all these agencies.

Product information was gathered primarily from the literature and industry sources. The availability of data on the chemical breakdown of products is limited. ASTM (American Society for Testing and Materials) standards were relied upon for some of this information.

The most readily available information was on the gross refining and wastewater processes used at each of the refineries. Refineries were relied upon to supply specific numbers on processes (e.g., process volumes and retention times).

Specific data on the chemical composition of the various influent streams to individual refinery wastewater treatment plants is singularly lacking. The refiners are not required to report this kind of information and so do not routinely analyze influent streams.

The most reliable information on refinery effluent characteristics is the monthly effluent reports submitted by the refineries to the State Department of Ecology (DOE). These reports provide daily and monthly figures on levels of the following effluent parameters:

Figure 2

Sample Questionnaire

REFINERY INFORMATION NEEDED

Waste Treatment

1. Retention times for various treatment processes.
2. Average retention time for final holding pond.

Storm and Ballast Water Volumes

1. Monthly and annual average and maximum flow.

Crude Oil

1. Any information on crudes types - sources.
2. Any information on volume of each crude.
3. Pipeline vs. marine transport.

Influent Characteristics

1. Parameters: total suspended solids, NH_3, pH, sulfide, COD, BOD, phenols, hexavalent chromium, total chromium, fecal coliform, oil and grease.
2. Any further breakdown of oil and grease to hydrocarbon types.

Products

1. Types of products - and amounts or relative percentages.
2. Mode of transport - relative amounts.
3. Any information on product characteristics: hydrocarbon composition mainly; ASTM specifications.

Effluent

1. Any specific hydrocarbon breakdown of oil and grease.
2. Oil removal efficiency of treatment plant.
3. Concentration of oil and grease after final clarification pond (prior to final holding pond).

Total Suspended Solids (TSS)
Ammonia as Nitrogen
pH
Oil and Grease
Sulfide
Chemical Oxygen Demand (COD)
Biochemical Oxygen Demand (BOD)
Hexavalent Chromium
Total Chromium
Fecal Coliform Bacteria
Temperature
Phenolic Compounds

It was found, in inquiries to all Washington State refineries, that no analyses of oil and grease are routinely performed to identify specific hydrocarbon compounds. The industry perspective is that recovery of as much oil as possible from the waste processing plant for re-processing in the refinery is a major function of the waste treatment process. The oil and grease fraction that does eventually leave the refinery via the final effluent has no practical value for the refiner and so is not analyzed.

The following sections of this report present the data collected for the study and reflect the environmental implications associated with this information.

II. OVERALL PETROLEUM IMPACTS ON WASHINGTON STATE

A. Current Petroleum Activities: The Refineries of Washington State

The United States is divided into five Petroleum Administration for Defense (PAD) Districts. Washington State is in PAD V, which also includes Oregon, California, Nevada, Arizona, Alaska, and Hawaii. The Pacific Northwest includes Idaho (which is in PAD IV), Oregon, and Washington.

In 1972, the Pacific Northwest consumed petroleum at the rate of 440,000 barrels per day (b/d). Of this, more than 60 percent was used for transportation--mostly gasoline for cars. More than half the total energy supply came from petroleum, and half of all the petroleum was consumed by households (includes private vehicle fuel consumption). Petroleum for private and public transportation accounted for one-third of all energy used.

The Pacific Northwest has no commercially productive oil fields as of today. The demand for petroleum products is met by refineries in Washington, California, Montana, and Utah. Refineries in Washington must import all the crude oil they process. Since construction of the Trans Mountain Pipeline from Edmonton, Alberta, to the four major refineries in northern Puget Sound, the principal source of crude oil for the Northwest has been Canada. Now, Canada is reducing its exports of crude oil to the U.S., and Washington refineries are becoming increasingly dependent on tankers for their crude supply.

There are six active refineries in Washington State. Together, their refining capacity is about 362,400 barrels per day. The four refineries in Skagit and Whatcom counties represent about 94 percent (336,500 b/d) of this total capacity. Two of these refineries are located near Anacortes (Shell and Texaco) and two are in the Cherry Point-Ferndale area (ARCO and Mobil).

The remaining two active refineries are in Tacoma (U.S. Oil & Refining and Sound Refining). There is a small, inactive refinery (4,500 b/d capacity) at Richmond Beach that is owned by Standard Oil of California (SOCal). SOCal also owns property in the Cherry Point-Ferndale area on which a refinery might someday be located.

The ARCO refinery at Cherry Point is unique in that it was specially built to process North Slope crude and was designed to meet current and anticipated environmental standards. Selected characteristics of Washington refineries appear in Tables 1 and 2.

There are six primary marine terminals for receiving crude oil in Washington State. These are located at Anacortes, Cherry Point-Ferndale, and

Table 1

Selected Characteristics of Major Washington Refineries, 1974

Item	Atlantic Richfield Co.	Mobil Oil Co.	Shell Oil Co.	Texaco Inc.
Year Built	1972	1954	1955	1958
Acreage	1200	800	800	850
Present Capacity (1000 barrels per calendar day)	96	71.5	91	78
Potential Capacity (1000 barrels per calendar day)	300	200	200	210
Present Crude Storage (days of refining capacity)	20	8	7	20
Employment	380	300	400	400
Water (Million gallons per day)	3.7	4.2	4.0	3.8

Source: (21)§

§Throughout this volume references are denoted by a one- or two-digit number in ( ). This number corresponds to a complete reference listing in Section III.A.

Table 2

Capacity of Petroleum Refineries in the Pacific Northwest, January 1, 1976

Company	Location	Crude Distillation Capacity bbls/cal.day	Process Units and Other Products
Atlantic Richfield Company	Ferndale	96,000	Cat. Rf., Hydro., Cok.
Mobil Oil Corporation	Ferndale	71,500	Cat. Ck., Cat. Rf., Thml. Ck., Alk.
Shell Oil Company	Anacortes	91,000	Cat. Ck., Cat. Rf., Alk.
Texaco Inc.	Anacortes	78,000	Cat. Ck., Cat. Rf., Alk.
U.S. Oil & Refining	Tacoma	21,400	Cat. Rf., Asphalt
Sound Refining	Tacoma	4,500	Asphalt, Lubricants

Cat. Ck.	. . . . . Catalytic Cracking
Cat. Rf.	. . . . . Catalytic Reforming
Hydro.	. . . . . Hydrocracking
Thml. Ck.	. . . . . Thermal Cracking
Cok.	. . . . . Coking
Alk.	. . . . . Alkylation

Tacoma (see Table 3). There are more than 18 terminals at ten Puget Sound ports for handling refined products (see Table 4).

Most of the maritime commerce in bulk petroleum is conducted through Seattle, Anacortes, Cherry Point-Ferndale, and Tacoma. In 1974, for example, Anacortes, Cherry Point-Ferndale, and Tacoma received more than 5 million short tons§ of the Washington marine total of 5.6 million short tons of crude oil. This crude oil import activity represented nearly 12 percent of the 1974 total commodity traffic on Puget Sound. These three ports plus Seattle imported and exported over 8 million of the 1974 marine total of 9.2 million short tons of refined products. Table 5 presents a breakdown of waterborne transport of bulk petroleum and petroleum products within Puget Sound for the years 1973 and 1974.

Relative to Seattle, Tacoma handles significantly greater amounts of crude but much less refined products. The crude serves Tacoma's refineries. There are no refineries at Seattle, but Seattle is Western Washington's major product-use center.

The system for supplying crude oil to Washington's refineries is via the Trans Mountain pipeline and by vessel (see Figure 3). The Trans Mountain pipeline serves the four major refineries in northern Puget Sound. In rough figures, these refineries have historically received about 200,000 barrels per day via the pipeline and about 100,000 b/d via tanker. Now, Canada is decreasing the pipeline flow (shut-off by 1977 for Puget Sound) and this deficit is being made up by increased tanker traffic.

The refined products distribution system is shown in Figure 4. The principal products consumed in the Pacific Northwest are gasoline, kerosene, jet fuel, naphtha, distillate fuel oils (including home heating oil and diesel), residual fuel oils (for industrial uses), asphalt, and lubricants. The four major refineries transfer their products through the Olympic pipeline, which extends from Cherry Point to Eugene, Oregon, and by vessels and barges to points within and outside Puget Sound. They ship relatively insignificant amounts by truck or tank car. The two Tacoma refineries produce mostly asphalt and lubricants, which they ship by vessel, truck, and tank car.

B. Crude Oils Utilized in Puget Sound

1. Introduction

The combined maximum capacity of petroleum refineries in Washington in 1976 is 362,400 barrels per calendar day (BPCD). Although it is possible to exceed this rated capacity (the ARCO refinery has been averaging over

---

§There are between 5.9 and 7.7 barrels of crude oil per short ton, depending on the crude's specific gravity.

Table 3

Existing Marine Terminals for Crude Oil, State of Washington

	Owner & Location:					
	ARCO§ Cherry Point	Mobil† Ferndale	Shell Anacortes	Texaco Anacortes	U.S. Oil & Refining Tacoma	Sound Refining Tacoma
Exposure to weather:	Exposed	Exposed	Sheltered	Sheltered	Sheltered	Sheltered
Exposure to waves:	Exposed	On shelf	Sheltered	Sheltered	Sheltered	Sheltered
Controlling depth of approach channel:	N.A.	N.A.	54'/84'††	54'/84'††	35'	30'
Depth at principal berth:	65'	45'	45'	45'‡	40'	30'
Max vessel dwt:	125,000	60,000	60,000	60,000‡	35,000	20,000
Length of principal berth:	970'	850'	925'	1,100'	840'	840'
Auxiliary berth(s):	None	1 (Barge)	1 (Barge)	1 (Tanker) 1 (Barge)	1 (Tanker	None
Length of trestle to shore:	2,000'	2,100'	3,500'	5,600'	100'	0'
Oil transfer system:	Steel loading arms	Hoses	Hoses	Hoses	Hoses	Hoses

Source: (21)

§A permanent floating oil spill confinement boom is installed.

†Turning dolphin is installed to permit deberthing without tug assistance.

††54' depth is that applicable to Guemes Channel; 84' is controlling depth east of Guemes Island.

‡Design permits dredging to 50' water depth, to accommodate vessels up to 85,000 dwt.

N.A. Not applicable

Table 4

Bulk Petroleum Receiving Terminals, Puget Sound and Vicinity

Port	Operator	Location	Type	No. Facilities Receiving Bulk Petroleum
Anacortes	Shell Oil Co. Texaco, Inc.	Fidalgo Island Fidalgo Island	Refinery/Pier/Tanks Refinery/Pier/Tanks	5
Bellingham	Std. Oil Co. of Calif.	Whatcom Creek Waterway	Pier/Tanks§	8
Edmonds	Union Oil Co. of Calif.	Edwards Point	Pier/Tanks§	3
Everett	Mobil Oil Corp.	Port of Everett	Pier/Tanks§	7
Ferndale	Mobil Oil Corp. Atlantic Richfield Co.	Cherry Point Cherry Point	Refinery/Pier/Tanks Refinery/Pier/Tanks	2
Olympia	Std. Oil Co. of Calif.	Olympia	Pier/Tanks§	6
Port Angeles	Std. Oil Co. of Calif.	Port Angeles	Pier/Tanks§	11
Richmond Beach	Shell Oil Co. Std. Oil Co. of Calif.	Point Wells Point Wells	Pier/Tanks§ Pier/Tanks§	2
Seattle	Atlantic Richfield Co. Mobil Oil Corp. Phillips Petroleum Co. Shell Oil Co. Std. Oil Co. of Calif. Union Oil Co. of Calif.	Pier 11, Harbor Island Pier 15, Harbor Island Pier 34, East Waterway Pier 19, Harbor Island Pier 32, East Waterway Pier 70	Pier/Tanks§ Pier/Tanks§ Pier/Tanks§ Pier/Tanks§ Pier/Tanks§ Pier/Tanks§	23
Tacoma	U.S. Oil & Refining Co. Sound Refining, Inc.	Blair Waterway Hylebos Waterway	Refinery/Pier/Tanks Refinery/Pier/Tanks	16

§These terminals handle only refined products.

Source: (21)

Table 5

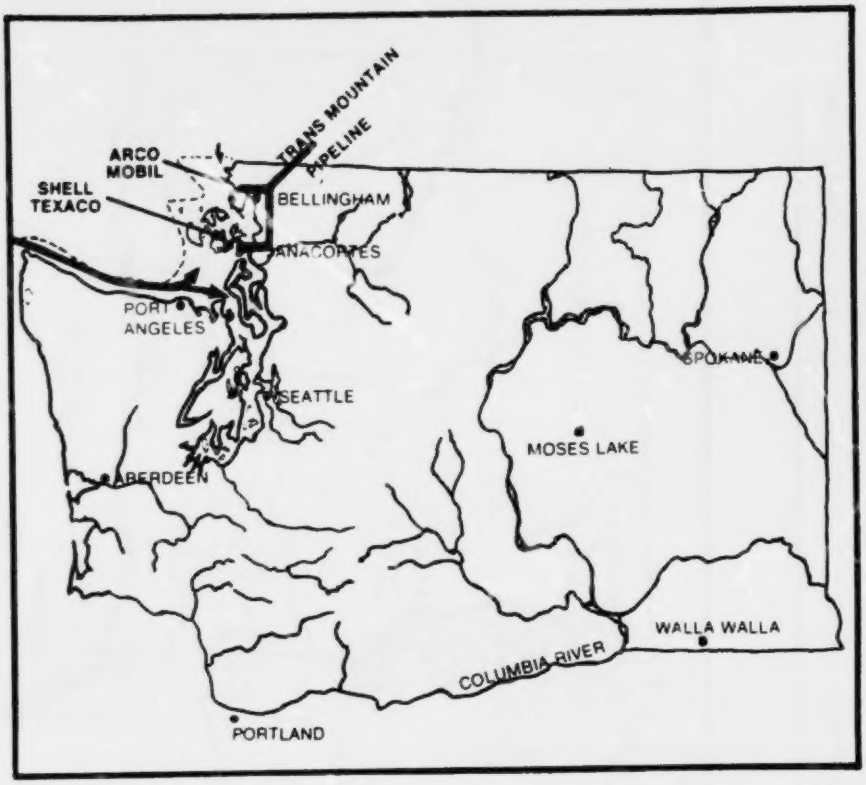
Total Waterborne Transport of Petroleum and Petroleum Products (In 1000 short tons) Throughout Puget Sound

Petroleum and Petroleum Products	1973	1974
Crude Oil	3,297	5,602
Total Petroleum Products	9,770	7,357
Gasoline	3,268	2,338
Jet Fuel	614	467
Kerosene	427	288
Distillate Fuel Oil	3,255	1,840
Residual Fuel Oil	1,766	2,051
Lubricating Oil and Grease	171	128
Naphtha, Petroleum Solvents	33	74
Asphalt, Tar and Pitches	236	171
Total Petroleum and Petroleum Products	13,067	12,959

Source: (28, 29)

Figure 3

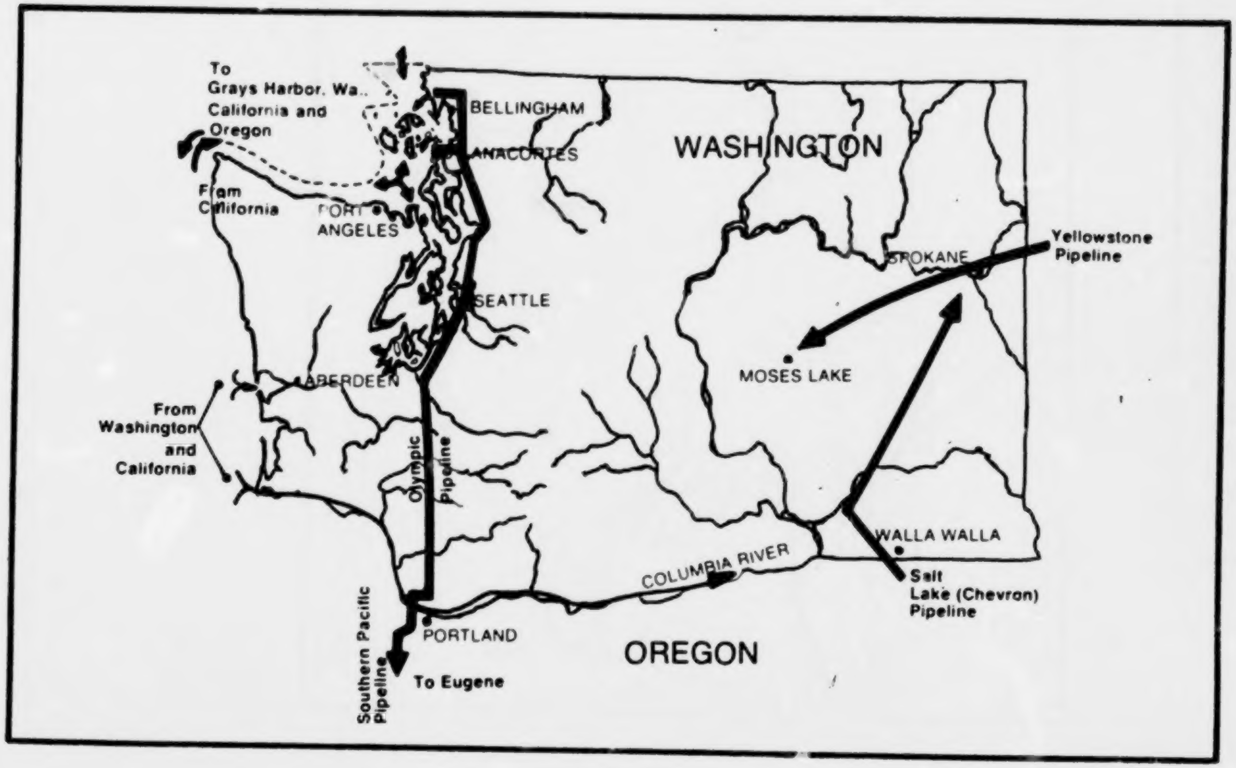
Waterborne and Pipeline Elements of the Crude Oil Supply System in Washington


TRANS MOUNTAIN PIPELINE
ARCO
MOBIL
SHELL
TEXACO
BELLINGHAM
ANACORTES
PORT ANGELES
SEATTLE
SPOKANE
MOSES LAKE
ABERDEEN
WALLA WALLA
COLUMBIA RIVER
PORTLAND

Source: (21)

Figure 4

Waterborne and Pipeline Elements of the Refined Product Distribution System in Washington


To
Grays Harbor, Wa.,
California and
Oregon
From
California
PORT
ANGELES
BELLINGHAM
ANACORTES
SEATTLE
ABERDEEN
From
Washington
and
California
Olympic
Pipeline
Southern Pacific
Pipeline
To Eugene
PORTLAND
WASHINGTON
OREGON
COLUMBIA RIVER
MOSES LAKE
SPOKANE
Yellowstone
Pipeline
WALLA WALLA
Salt
Lake (Chevron)
Pipeline

Source: (21)

100,000 BPCD of crude oil feedstock for the first half of 1976) rarely have the refineries operated at peak capacity. Due largely to cutbacks in the supply of Canadian crude oil, Mobil, Shell and Texaco have been operating below capacity. The Shell refinery at Anacortes has occasionally operated at a low of 80 percent of capacity. Sound Refining and U.S. Oil & Refining also rarely operate at capacity. Sound Refining particularly has had economic difficulties recently and has been operating at less than 70 percent of its rated 4,500 BPCD capacity. Also due to the economics of utilizing a heavy asphaltic crude (heat must be applied to make the crude oil flow), Sound Refining shuts down in winter and has often been shut down for five or six months of each year. Thus the average annual operation of the six Washington refineries since 1974 is around 330,000 BPCD, approximately 90 percent of the rated maximum capacity.

The crude oils utilized by the refineries are received either by pipeline or marine transport. Mobil, ARCO, Shell, and Texaco are all connected to the Trans Mountain pipeline which supplies Canadian crudes from Edmonton, Alberta and other Canadian oil fields. The two small Tacoma refineries are not connected to any crude pipeline and receive all of their crude oil by waterborne transport. The four major refineries also receive a portion of their crude oil supply by tanker.

2. Marine Transport of Crude Oil

Marine transport of crude oil into Puget Sound has been increasing for a number of years. In the peak year 1972, the Trans Mountain pipeline accounted for more than 80 percent of the crude oil received, with the remaining 45,000 barrels per day arriving by barge or tanker. Since then waterborne transport of crude oil has risen to more than 60 percent with the onset of the Canadian phase-out of crude oil exports (Table 6). By early 1977, according to the proposed Federal Energy Administration (FEA) allocation of Canadian crude, the Puget Sound refineries will be totally dependent on marine transportation for crude oil.

Waterborne transport of petroleum is monitored and categorized in detail by the U.S. Army Corps of Engineers and published in November of each following year. Hence detailed information regarding receipts of crude oil in 1975 and 1976 is not yet available, although values for the total amount of imported crude are available from the refinery effluent reports to the DOE. Table 7 shows the receipts and shipments of crude oil in Puget Sound as a total, and by port, with each subdivided to indicate foreign, coastal, internal and local transport in short tons for 1973 and 1974. The "Total" category is for all ports in Puget Sound (defined here to include the Strait of Juan de Fuca beginning at Neah Bay) which receive crude. The Ports of Tacoma, Seattle, Anacortes and Bellingham are the principal recipients of crude oil in Puget Sound. Bellingham receipts are delivered actually to the docks of ARCO and Mobil at Cherry Point and Ferndale, respectively. Seattle has no refineries but does have a number of storage tank farms and uses some crudes for industrial heating fuel. The subcategory "Coastal" represents all domestic marine traffic that enters Puget Sound. As often as possible specific states are named as shipping ports or destinations of the crude. Movement of crude oil within Puget Sound is indicated under "Internal". "Local" transport is within an individual harbor or port and has been

Table 6

Comparison of Pipeline and Marine Transport of Crude Oil Imports to Washington Refineries

Date	Mode of Transport Pipeline	Marine
1974	66%	34%
1975	60%	40%
1976 First Half	37%	63%
Second Half§	20%	80%
1977§	0%	100%

§projections based on proposed FEA allocations

Table 7

Waterborne Transport of Crude Oil (in Short Tons) in Puget Sound[§]

Shipping Port or Destination	Receipts		Shipments	
	1973	1974	1973	1974
Total				
Foreign	2,187,767	4,684,330	0	0
Coastal	1,048,369	888,550	58,009	22,930
Internal	3,106	0	3,106	0
Local	0	6,029	-	-
Tacoma				
Foreign	365,175	201,451	0	0
California	281,737	295,332	4,740	0
Alaska	0	54,000	0	0
Internal	0	0	3,106	0
Local	0	6,029	-	-
Seattle				
Foreign	53,022	57,971	0	0
California	20,031	4,394	0	0
Internal	3,106	0	0	0
Anacortes				
Foreign	93,735	1,429,614	0	0
California	0	74,353	30,402	0
Alaska	208,253	89,302	0	0
Texas	0	24,192	0	0
Bellingham				
Foreign	1,675,835	2,995,294	0	0
California	124,851	96,442	22,867	22,930
Alaska	413,497	250,545	0	0

[§] For conversion to barrels, there are 5.9 to 7.7 barrels of crude oil per short ton depending on the specific gravity of the particular crude.

Source: (28, 29)

arbitrarily listed under receipts ("-" appears under shipments). No crude originates in Washington, but some tankers unload a portion of their crude oil in Puget Sound before proceeding to refineries in California, thus appearing as shipments of crude.

Most of the marine imported crude is from foreign sources, with smaller amounts from Alaska, California, and occasionally Texas or the East Coast. The percentage of marine transport of foreign versus domestic crude oil has risen from 67 percent in 1972 to more than 80 percent in 1974. With the cutback of Canadian crude, local Puget Sound refineries expect to be importing even more foreign crude by marine transport, although the availability of Alaskan North Slope crude oils may shift the dependency on foreign sources of crudes.

The types and sources of crude oils received by marine transport for the past three years are indicated in Table 8. Sound Refining in Tacoma receives a mix of heavy crudes: San Joaquin and Santa Maria, from California. U.S. Oil & Refining utilizes two crudes also: Indonesian crude and a southern California coastal crude. These refineries will be unaffected by the phasing out of Canadian crude. Sound Refining has experienced a recent change in management and is considering expansion of operations and the utilization of different crude sources and types. The crudes imported across the docks of the four major refineries are indicated in Table 9 by refinery. Some crude oils are utilized by more than one refinery. This is due to the fact that there is a strong similarity between the refineries and the processes they employ, since all but the ARCO refinery were designed to handle light, sweet crudes. The ARCO plant was designed to handle crudes with higher sulfur content, specifically Alaskan North Slope crude.

The four major refineries recently have indicated they will use Alaskan North Slope crude to at least some extent for feedstock. Both Texaco and Mobil have previously announced the possibility of enlarging product handling facilities to enable them to refine the heavier North Slope crude. Shell also will utilize North Slope crude, with the exact input being limited by the refinery design, which favors lighter, sweeter crudes. The maximum percentage of the total refinery feedstock will depend on the other crudes being processed, but Shell estimates that it will be much less than 50 percent. The ARCO refinery will utilize nearly 100 percent Alaskan North Slope crude. Some sweeter crudes may occasionally be used to produce very low sulfur fuels. The present design of the Sound Refining refinery is not capable of handling the Alaskan crude and U.S. Oil & Refining is also not likely to utilize North Slope crude when it becomes available.

3. Pipeline Transport of Crude

The Trans Mountain pipeline has supplied U.S. refineries with Canadian crude oils since the first refinery was built in 1954. The 893 miles of pipeline, originating in Edmonton, Alberta, includes nearly 64 miles in the U.S. which supplies the refineries at Ferndale, Cherry Point, and Anacortes (see Figure 5). The pipeline company is solely a carrier, providing oil producing companies with an economical means of transportation from the areas of production to refining centers. Sixteen independent Canadian companies

Table 8

Types and Sources of Crude Oils Received from 1974-1976 by Marine Transport by Puget Sound Refineries

Domestic

- Alaska
  - Cook Inlet
- California
  - San Joaquin
  - Santa Maria
  - San Ardo

Saudi Arabia/Iran

- Arabian Light
- Berri
- Iranian Light
- Iranian Heavy
- Sassan

Abu Dhabi

- Murban

Indonesia/Malaysia

- Attaka
- Minas
- Arjuna
- Walio Export Mix
- Bekapai
- Poleng
- Labuan Light
- Katapa

Ecuador/Venezuela

- Lagomedio
- Oriente

Nigeria

- Brass River
- Qua Iboe
- Bonny Light

Table 9

The Major Crude Oils Utilized by the Puget Sound Refineries from 1974-1976

MOBIL

Canadian (Pipeline)
Cook Inlet
California Coastal
Murban
Walio Export Mix
Berri
Minas
Lagomedio
Iranian Light
Oriente
Attaka
Arjuna
Bonny Light

TEXACO

Canadian (Pipeline)
Minas
Attaka
Oriente
Lagomedio
Murban

SOUND REFINING

San Joaquin
Santa Maria

ARCO

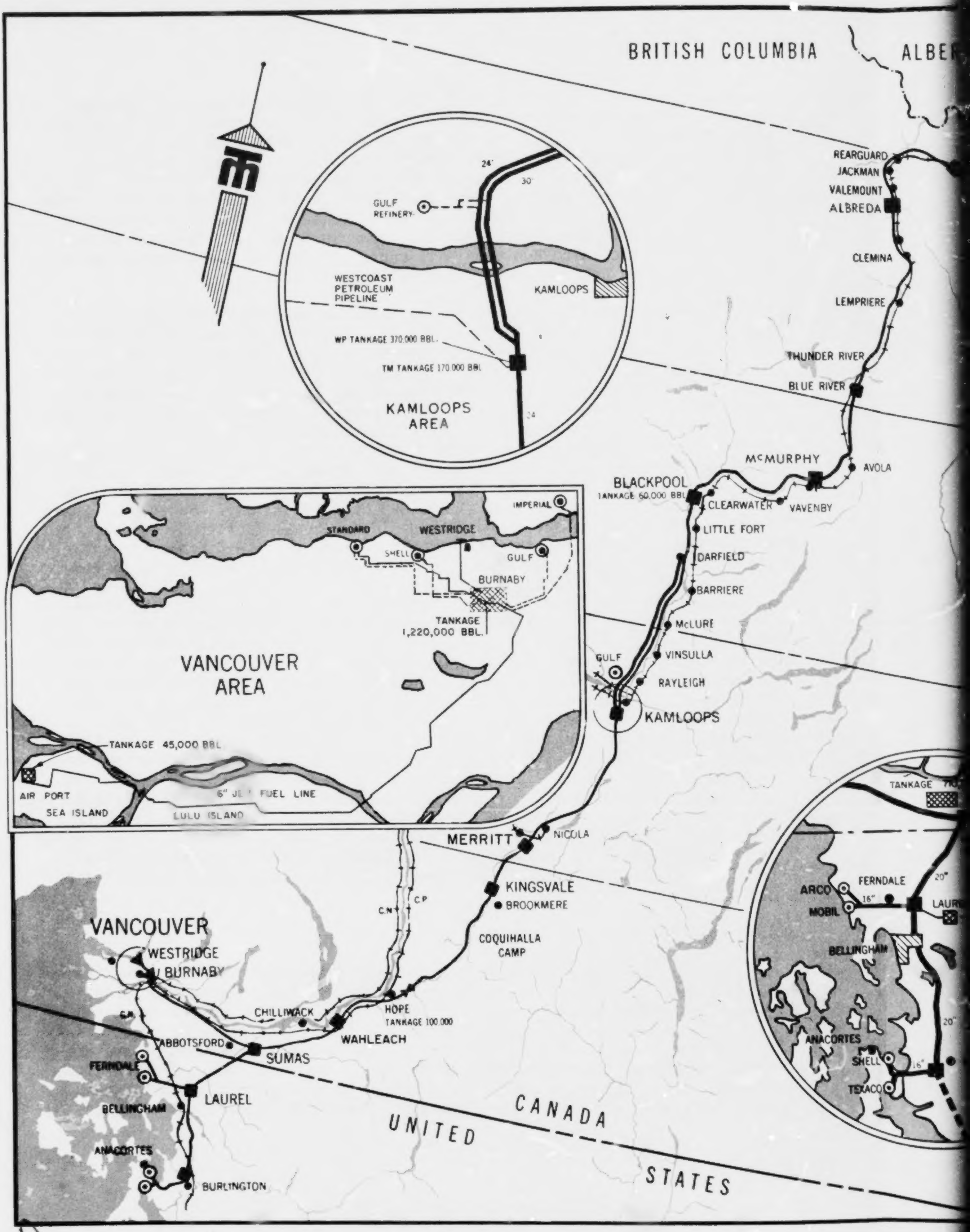
Canadian (Pipeline)
Iranian Light
Iranian Heavy
Murban
Arabian Light
Sassan
Cook Inlet

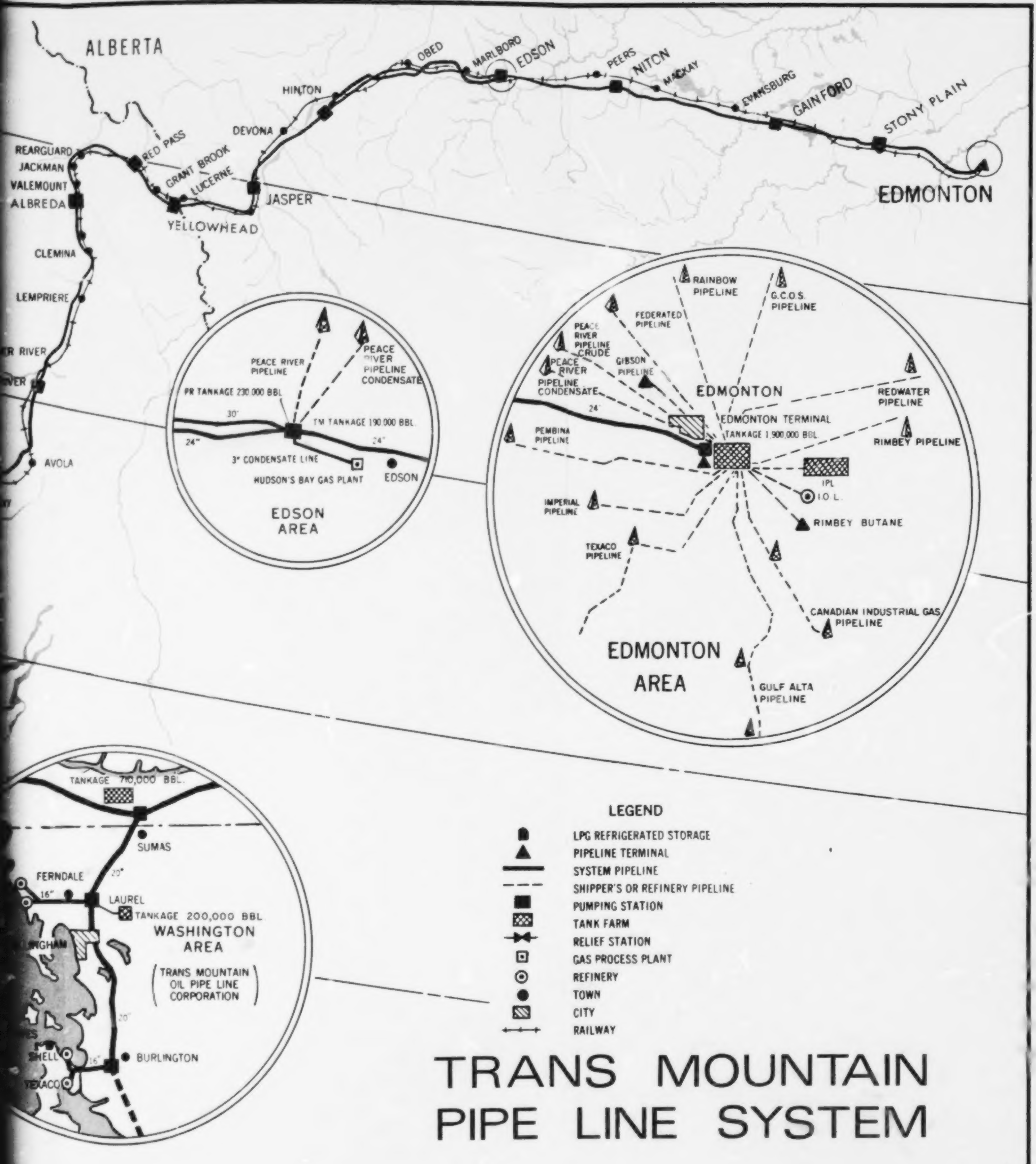
SHELL

Canadian (Pipeline)
Cook Inlet
Walio Export Mix
Minas
Bekapai
Poleng
Labuan Light
Brass River
Qua Iboe
Murban
Oriente

U.S. OIL & REFINING

Katapa
San Ardo
Cook Inlet
Attaka


BRITISH COLUMBIA
ALBER
REARGUARD
JACKMAN
VALEMOUNT
ALBREDA
CLEMINA
LEMPRIERE
THUNDER RIVER
BLUE RIVER
McMURPHY
AVOLA
BLACKPOOL
TANKAGE 60,000 BBL
CLEARWATER
VAVENBY
LITTLE FORT
DARFIELD
BARRIERE
McLURE
VINSULLA
RAYLEIGH
GULF
KAMLOOPS
24"
30"
GULF REFINERY
WESTCOAST PETROLEUM PIPELINE
KAMLOOPS
WP TANKAGE 370,000 BBL
TM TANKAGE 170,000 BBL
24
KAMLOOPS AREA
IMPERIAL
STANDARD
WESTRIDGE
SHELL
GULF
BURNABY
TANKAGE 1,220,000 BBL.
VANCOUVER AREA
TANKAGE 45,000 BBL
AIR PORT
SEA ISLAND
6" JET FUEL LINE
LULU ISLAND
MERRITT
NICOLA
KINGSVALE
BROOKMERE
COQUIHALLA CAMP
C.N
C.P
VANCOUVER
WESTRIDGE
BURNABY
C.P.
CHILLIWACK
HOPE
TANKAGE 100,000
WAHLEACH
ABBOTSFORD
SUMAS
FERNDALE
LAUREL
BELLINGHAM
ANACORTES
BURLINGTON
CANADA
UNITED
STATES
TANKAGE
FERNDALE
20"
ARCO
MOBIL
16"
LAUR
BELLINGHAM
20"
ANACORTES
SHELL
16"
TEXACO


ALBERTA
OBED
MARLBORO
EDSON
PEERS
NITON
MACKAY
EVANSBURG
GAINFORD
STONY PLAIN
HINTON
DEVONA
EDMONTON
REARGUARD
JACKMAN
VALEMOUNT
ALBREDA
RED PASS
GRANT BROOK
LUCERNE
JASPER
YELLOWHEAD
CLEMINA
LEMPRIERE
AVOLA
PEACE RIVER PIPELINE
PEACE RIVER PIPELINE CONDENSATE
PR TANKAGE 230,000 BBL
30"
24"
TM TANKAGE 190,000 BBL
24"
3" CONDENSATE LINE
HUDSON'S BAY GAS PLANT
EDSON
EDSON AREA
RAINBOW PIPELINE
G.C.O.S. PIPELINE
FEDERATED PIPELINE
PEACE RIVER PIPELINE CRUDE
GIBSON PIPELINE
PEACE RIVER PIPELINE CONDENSATE
24"
EDMONTON
REDWATER PIPELINE
EDMONTON TERMINAL
TANKAGE 1,900,000 BBL
PEMBINA PIPELINE
RIMBEY PIPELINE
IPL
I.O.L.
IMPERIAL PIPELINE
RIMBEY BUTANE
TEXACO PIPELINE
CANADIAN INDUSTRIAL GAS PIPELINE
EDMONTON AREA
GULF ALTA PIPELINE
TANKAGE 710,000 BBL.
SUMAS
FERNDALE
20"
16"
LAUREL
TANKAGE 200,000 BBL
WASHINGTON AREA
(TRANS MOUNTAIN OIL PIPE LINE CORPORATION)
20"
SHELL
16"
BURLINGTON
TEXACO
LEGEND
LPG REFRIGERATED STORAGE
PIPELINE TERMINAL
SYSTEM PIPELINE
SHIPPER'S OR REFINERY PIPELINE
PUMPING STATION
TANK FARM
RELIEF STATION
GAS PROCESS PLANT
REFINERY
TOWN
CITY
RAILWAY

TRANS MOUNTAIN PIPE LINE SYSTEM

B

produce oil which is transported by the Trans Mountain Pipe Line Company. The U.S. refineries receive crude oil, condensates and butane via the pipeline (Table 10). The pipeline company receives orders from the refineries for specific blends of available Canadian crudes, condensates and butane, and transports them in distinct batches to the appropriate refinery. The volume of the crude received from Canada through the pipeline reached a peak of 277,000 BPCD in 1972. The deliveries of Canadian crude oils (including condensates and butane) since 1973 are shown in Table 11. This volume has been steadily declining and soon will cease entirely as the Canadian government attempts to achieve energy self reliance by 1981.

Two major factors have caused the Canadian government to examine and change its oil export and import policies. The Arab oil embargo forced a reevaluation of the short and long-term security of the primary energy supply for the eastern cities of Canada. The revenue from export taxes on Canadian crudes going to the U.S. was being used to pay for the import of crude oil required by the eastern provinces. With imports no longer readily available, the supply of crude oil to the eastern cities was greatly imperiled. The second factor influencing the decision was a series of studies which evaluated Canada's future crude oil supply and demand balance. These studies concluded that by 1983 the demand would be greater than the production, resulting in a domestic shortage of 100,000 barrels per day. Because of these factors, the Canadian government has decided to phase out crude oil exports to the U.S., along with other efforts to achieve self-sufficiency in oil. The process of phasing out exports of oil, which was originally to be completed by 1983, will be accomplished by 1981. The Canadian export plan authorizes the U.S. to allocate the export volumes to specific U.S. refineries as it desires. Recent actions by the Federal Energy Administration (FEA) have designated the Puget Sound refineries as second priority refiners based on the dependency upon Canadian crude sources and their capability to replace Canadian crude with crude from other sources. First priority refiners are those which utilized at least 25 percent by volume of Canadian crude oils during the period from November 1, 1974, through October 31, 1975, and possess no current capacity to replace Canadian crudes due to a demonstrated lack of access to domestic pipelines, storage or port facilities or any other methods of crude supply. Second priority refiners are "those which do not qualify as first priority refiners" (33). Because of the preestablished access to marine importation of crude oils, the four Puget Sound refineries receiving crude oil from Canada (Mobil, ARCO, Texaco, Shell) were designated second priority refineries. The allocation of Canadian crude proposed by FEA will result in the complete cutoff of Canadian crude to Washington refineries by early 1977.

4. Potential Crude Oil Supply

As the Canadian crude supply is cut back, the Puget Sound refineries must turn to other sources of crude for feedstock. In some instances, larger quantities of the crudes presently being utilized may be sufficient. However, new sources of light, sweet crude oil most certainly will be necessary. Some of the crudes presently imported by the four major refineries are among the world's top fifteen imported crude oils. These include: Arabian Light, Iranian Light, Lagomedio, Qua Iboe, Murban, Bonny Light and Iranian Heavy. Thus, obtaining additional quantities of these high-demand crudes may be

Table 10

Canadian Crudes and Other Feedstock Received via the Trans Mountain Pipeline by the Puget Sound Refineries

Crude Oils

Rainbow
Texaco
Federated Mix
Peace River
Ellerslie

Condensates

Carson Creek
Cabob
Worsley
Windfall
Edson
Taylor

Butane

Table 11

Deliveries of Canadian Crude Oil (BPD) to Washington State Refineries Via the Trans Mountain Pipeline

	1973	1974	1975	1976 (6 months)
First Quarter	271,283	184,108	187,306	123,899
Second Quarter	256,769	200,478	173,780	101,733
Third Quarter	265,251	201,696	175,446	
Fourth Quarter	235,471	220,456	180,995	
Annual Average	257,118	201,784	179,313	112,816
Percent Natural Gas Liquids	4.5	5.2	5.2	5.1

Source: (22, 23, 25, 26)

difficult. Furthermore, the process configuration of each refinery places a limit on the types of crudes and blends of crudes which will yield the desired product output. So crudes replacing the Canadian oil will have to be similar to those already being used unless the refineries are modified and expanded. In affidavits from the refineries to the FEA, each refinery provided some information regarding potential replacement crude oils. A list of the types and sources of crudes under consideration for replacing the diminishing Canadian crude supply is shown in Table 12. Of these 34 crude oils, 10 are among the world's top 15 imported crudes: Zuetina, Forcados, Es Sider, Cabinda, Lagomedio, Qua Iboe, Murban, Arzew, Zarzaitine and Bonny Light, so other suitable Indonesian, Nigerian, Libyan and Algerian crudes must also be considered. The specific blends of crude which will be utilized will be determined by crude oil economics.

5. Chemical Composition and Characteristics of Crude Oil

Crude petroleum is a mixture of chemical compounds derived from biological material that has accumulated in an area and been subjected to physical, chemical and biological processes for millions of years. The physical and chemical composition of petroleum varies greatly, depending upon where it is obtained. Even samples of crude taken at different depths or different times from the same field may have some noticeable differences. Note the variations in sulfur content, gravity, pour point and other characteristics found in crude assays made in a single oil field at different depths, shown in Tables 13(a), (b), and (c). There is tremendous variability in physical appearance of different crude oils, which is controlled by the chemical composition. Colors range from water-clear to black, with many shades of red, orange, green and brown in between. Specific gravities may vary from 0.70 to 1.00. Other physical properties also may vary greatly, including viscosity (0.6 to over 1,000 centipoise), surface tension (20 to 27 dynes per centimeter) and pour point temperature (-65°F to +65°F).

Crude oils are often described in terms of their API gravity and sulfur content, as heavy or light and sweet or sour. These categories are not well defined and may be simply relative to specific crudes being described. Generally API gravities range from 10.3 to 44.3. Light crudes are usually those over 30-32, while heavy crudes often have gravities below 20. Descriptions of crudes in the intermediate range of 20-32 are very subjective, but the intermediates are often simply labeled medium crudes. Sulfur content in crude oils may range from around 0.04 to 6 percent. However, this is not totally indicative of whether a crude oil is considered to be sweet or sour, because the hydrogen sulfide and mercaptan content is the true basis for this type of description. Very often though, sour crudes are categorized as having greater than three percent sulfur content and sweet crudes as having less than one percent. The middle range crudes are not well designated and often will vary with respect to which crude oils are being compared. Alaskan North Slope crude has a sulfur content of about one percent, but is usually labeled sour when compared to the sweet Canadian and other crudes presently being used by Puget Sound refineries.

The chemical composition of crude oil also is quite complex. Crude oils contain many tens of thousands of compounds, including hydrocarbons; sulfur-, oxygen-, and nitrogen-containing compounds, and metallo-organic

Table 12

Types and Sources of Crude Oils Under Consideration by Puget Sound Refineries for Replacement of Canadian Crude Oils

Domestic

- Alaska
  - Cook Inlet
  - North Slope

Nigeria

- Qua Iboe
- Forcados
- Brass River
- Bonny Light
- Escravos
- Pennington

Libya

- Zuetina
- Es Sider
- Bu Attifel
- Brega
- Sarir
- Amna

Ecuador/Venezuela

- Oriente
- Lagomedio

Indonesia/Malaysia

- Arjuna
- Attaka
- Bekapai
- Cinta
- Labuan Light
- Minas
- Poleng
- Badak
- Seppinggan
- Bunju
- Handil

Algeria

- Arzew
- Zarzaitine
- Hassi Messaoud

Gabon/Angola

- Gamba
- Anguille
- Cabinda

Abu Dhabi

- Murban

Table 13(a)

Characterization of Fenn-Big Valley Crude, Taken from 2,514-2,547 Feet

Bureau of Mines Bartlesville Laboratory
Sample 51029

Item 126

IDENTIFICATION

Fenn-Big Valley field
D-2, Devonian
2,514 - 2,547 feet

North America
Canada
Alberta

GENERAL CHARACTERISTICS

Gravity, specific, 0.858
Gravity, ° API, 33.4
Pour point, ° F., 20
Sulfur, percent, 1.09
Color, brownish black
Viscosity, Saybolt Universal at 77°F, 65 sec.; 100°F, 52 sec.
Nitrogen, percent, -

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 749 mm. Hg
First drop, 81 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	3.2	3.2)							
2	167	2.1	5.3)	0.647	87.2	-	1.38804	126.1		
3	212	4.4	9.7	.723	64.5	23	1.40143	130.0		
4	257	4.9	14.6	.749	57.4	26	1.41529	134.2		
5	302	4.3	18.9	.768	52.7	27	1.42547	136.6		
6	347	3.9	22.8	.788	48.1	30	1.43449	138.5		
7	392	3.5	26.3	.803	44.7	31	1.44423	141.2		
8	437	4.0	30.3	.818	41.5	33	1.45297	145.2		
9	482	4.1	34.4	.830	39.0	33	1.45980	148.3		
10	527	6.1	40.5	.844	36.2	35	1.46784	155.2		

STAGE 2—Distillation continued at 40 mm. Hg

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
11	392	2.4	42.9	0.851	34.8	34	1.47564	157.0	40	10
12	437	5.6	48.5	.862	32.7	36	1.48460	159.8	46	30
13	482	5.4	53.9	.877	29.9	39			58	50
14	527	4.7	58.6	.889	27.7	42			88	70
15	572	7.3	65.9	.904	25.0	46			180	85
Residuum		30.5	96.4	.980	12.9					

Carbon residue, Conradson: Residuum, 11.2 percent; crude, 3.9 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	9.7	0.681	76.3	
Total gasoline and naphtha	26.3	0.740	59.7	
Kerosine distillate	4.0	.818	41.5	
Gas oil	15.9	.846	35.8	
Nonviscous lubricating distillate	9.5	.867-.891	31.7-27.3	50-100
Medium lubricating distillate	8.1	.891-.908	27.3-24.3	100-200
Viscous lubricating distillate	2.1	.908-.918	24.3-22.6	Above 200
Residuum	30.5	.980	12.9	
Distillation loss	3.6			

Source: (31)

Table 13 (b)

Characterization of Fenn-Big Valley Crude, Taken from 2,581-2,694 Feet

Bureau of Mines Bartlesville Laboratory Item 128
Sample 51030

IDENTIFICATION

Fenn-Big Valley field	North America
D-2, Devonian	Canada
2,581 - 2,694 feet	Alberta

GENERAL CHARACTERISTICS

Gravity, specific, 0.854
Gravity, ° API, 34.2
Pour point, ° F, 35
Sulfur, percent, 0.71
Color, brownish black
Viscosity, Saybolt Universal at 100°F, 49 sec.
Nitrogen, percent, -

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure. 749 mm. Hg
First drop, 82 ° F.

Fraction No.	Cut temp. ° F	Percent	Sum. percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	2.7	2.7	0.663	81.9					
2	167	6.0	8.7	.692	73.6	18	1.38587	135.2		
3	212	4.7	13.4	.742	59.2	32	1.40992	131.4		
4	257	2.5	15.9	.758	55.2	30	1.41812	130.6		
5	302	3.3	19.2	.771	52.0	29	1.42496	133.6		
6	347	4.2	23.4	.786	48.5	29	1.43317	136.2		
7	392	3.7	27.1	.802	44.9	31	1.44264	139.7		
8	437	3.9	31.0	.818	41.5	33	1.45188	142.9		
9	482	4.3	35.3	.829	39.2	32	1.45806	145.6		
10	527	5.9	41.2	.841	36.8	33	1.46548	151.1		

Stage 2—Distillation continued at 40 mm. Hg

Fraction No.	Cut temp. ° F	Percent	Sum. percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
11	392	2.9	44.1	0.850	35.0	34	1.47396	156.6	41	15
12	437	6.2	50.3	.856	33.8	33	1.48204	159.0	46	30
13	482	5.3	55.6	.871	31.0	37			59	50
14	527	5.2	60.8	.884	28.6	40			91	65
15	572	6.8	67.6	.893	27.0	41			190	85
Residuum		29.0	96.6	.967	14.8					

Carbon residue, Conradson: Residuum, 8.7 percent; crude, 2.9 percent.

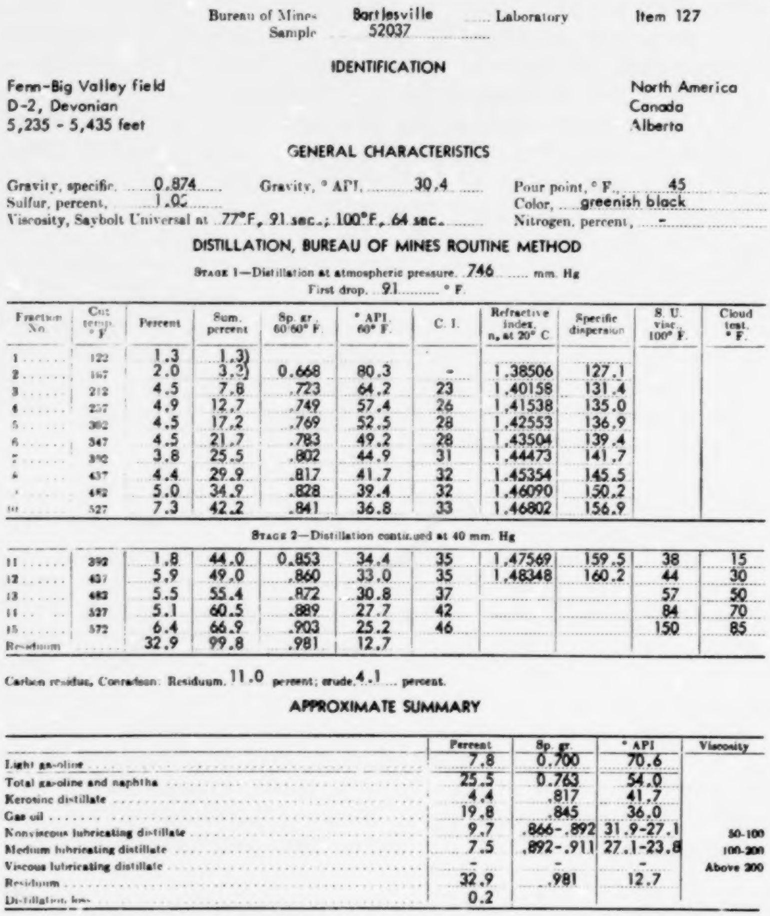
APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	13.4	0.704	69.5	
Total gasoline and naphtha	27.1	0.743	58.9	
Kerosine distillate	3.9	.818	41.5	
Gas oil	17.9	.843	36.4	
Nonviscous lubricating distillate	9.9	.860-.885	33.0-28.4	50-100
Medium lubricating distillate	6.1	.885-.894	28.4-26.8	100-200
Viscous lubricating distillate	2.7	.894-.899	26.8-25.9	Above 200
Residuum	29.0	.967	14.8	
Distillation loss	3.4			

Source: (31)

Table 13(c)

Characterization of Fenn-Big Valley Crude, Taken from 5,235-5,435



Bureau of Mines Bartlesville Laboratory
Sample 52037

Item 127

IDENTIFICATION

Fenn-Big Valley field
D-2, Devonian
5,235 - 5,435 feet

North America
Canada
Alberta

GENERAL CHARACTERISTICS

Gravity, specific, 0.874
Gravity, ° API, 30.4
Pour point, ° F., 45
Sulfur, percent, 1.03
Color, greenish black
Viscosity, Saybolt Universal at 77°F, 91 sec.; 100°F, 64 sec.
Nitrogen, percent, -

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 746 mm. Hg
First drop, 91 ° F.

Fraction No.	Cut temp. ° F	Percent	Sum. percent	Sp. gr. 60/60° F.	° API 60° F.	C. I.	Refractive index, n_D at 20° C	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	1.3	1.3)							
2	167	2.0	3.3)	0.668	80.3	-	1.38506	127.1		
3	212	4.5	7.8	.723	64.2	23	1.40158	131.4		
4	257	4.9	12.7	.749	57.4	26	1.41538	135.0		
5	302	4.5	17.2	.769	52.5	28	1.42553	136.9		
6	347	4.5	21.7	.783	49.2	28	1.43504	139.4		
7	392	3.8	25.5	.802	44.9	31	1.44473	141.7		
8	437	4.4	29.9	.817	41.7	32	1.45354	145.5		
9	482	5.0	34.9	.828	39.4	32	1.46090	150.2		
10	527	7.3	42.2	.841	36.8	33	1.46802	156.9		

STAGE 2—Distillation continued at 40 mm. Hg

Fraction No.	Cut temp. ° F	Percent	Sum. percent	Sp. gr. 60/60° F.	° API 60° F.	C. I.	Refractive index, n_D at 20° C	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
11	392	1.8	44.0	0.853	34.4	35	1.47569	159.5	38	15
12	437	5.9	49.0	.860	33.0	35	1.48348	160.2	44	30
13	482	5.5	55.4	.872	30.8	37			57	50
14	527	5.1	60.5	.889	27.7	42			84	70
15	572	6.4	66.9	.903	25.2	46			150	85
Residuum		32.9	99.8	.981	12.7					

Carbon residue, Conradson: Residuum, 11.0 percent; crude, 4.1 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	7.8	0.700	70.6	
Total gasoline and naphtha	25.5	0.763	54.0	
Kerosine distillate	4.4	.817	41.7	
Gas oil	19.8	.845	36.0	
Nonviscous lubricating distillate	9.7	.866-.892	31.9-27.1	50-100
Medium lubricating distillate	7.5	.892-.911	27.1-23.8	100-200
Viscous lubricating distillate	-	-	-	Above 200
Residuum	32.9	.981	12.7	
Distillation loss	0.2			

Source: (31)

compounds. The extreme complexity of crude oils has prevented a complete analysis of all the compounds present in any given crude. This complexity is thought to result from the molecular interactions which occurred when crude petroleum was formed. However, in general, hydrocarbon compounds comprise more than 75 percent of most crude oils. Assays of physical and chemical characteristics of the crude oils used in Puget Sound, or which potentially will be used in the near future, are in Appendix A and B.

Hydrocarbons in particular have such a wide range of molecular structures and molecular weights that no one method of analysis presently available offers an accurate assessment of all the specific compounds present. Even more troublesome is the fact that often the characterization provided by different analytical methods yields substantially different assessments. In a series of experiments analyzing the composition of crude oils, researchers at Massachusetts University found that results from fluorimetric analysis did not agree with the gas chromatographic results (27). A Nigerian light crude was found to contain 15 percent more hydrocarbons than an Iranian light crude according to the fluorimetric method; whereas, by gas chromatography, the Iranian light crude was indicated as having 80 percent more hydrocarbons than the Nigerian crude oil. It is highly probable that the two analytical techniques were actually assessing different chemical fractions of the crude oils. Thus one must be very careful when examining characterizations of crude oils and when comparisons are being made, to ensure that indicated differences are actual differences and not due to variations in analytical techniques.

Hydrocarbon compounds in crude oil may have from 1 to more than 70 carbon atoms and range in molecular weight from 16 (methane) to more than 20,000. Structurally they include alkanes, cycloalkanes and aromatic ring compounds. Olefins are generally absent in crude oils but are commonly present in refined products. The alkane hydrocarbons include both straight and branched carbon chains (Table 14). The cycloalkanes are a complex mixture of compounds including substituted and unsubstituted rings, with substituted ring compounds predominating (Table 15). The aromatic hydrocarbons in crude oils also are a very complex mixture of compounds. These include mono- and polyalkyl-benzenes, naphthalenes and polynuclear aromatic hydrocarbons with multiple alkyl substitutions (Table 16). Also included in this class of compounds are those hydrocarbons containing a mixture of aromatic and cycloalkane subunits, sometimes designated as naphthenoaromatics.

Crude oils differ mainly in the relative concentrations of the individual members of these classes of compounds (Table 17). The varying proportions of these compounds determine the physical, as well as the chemical properties of crude oils. An average of the gross compositional data on all world crude yields the following approximate composition for the "average" crude oil:

Table 14

Some Typical Paraffinic Hydrocarbons

	Formula	Melting Point (°F.)	Melting Point (°C.)	Boiling Point[a] (°F.)	Boiling Point[a] (°C.)	Sp. Gr. at °C.
Methane	CH_4	−300	−184	−258.5	−161.4	0.415 (liq.-164°)
Ethane	C_2H_6	−278	−172	−126.4	−88.3	0.446 (liq. 0°)
Propane	C_3H_8	−309.8	−189.9	−48.1	−44.5	0.536 (liq. 0°)
Butanes						
n-Butane	C_4H_{10}	−211.8	−135	31	−0.6	0.60 (0°)
Isobutane	C_4H_{10}	−229	−145	13.6	−10.2	0.559 (20°)
Pentanes						
n-Pentane	C_5H_{12}	−201.7	−129.9	96.8	36	0.626 (20°)
Isopentane (2-methylbutane)	C_5H_{12}	−254.8	−159.7	87.8	28	0.619 (20°)
2,2-Dimethylpropane	C_5H_{12}	−4	−20	49.1	9.5	0.613 (0°)
Hexanes						
n-Hexane	C_6H_{14}	−139.5	−95.3	155.7	68.7	0.660 (20°)
Isohexane (2-methylpentane)	C_6H_{14}	−244.6	−153.7	140.4	60.2	0.654 (20°)
3-Methylpentane	C_6H_{14}	−180.4	−118	145.8	63.2	0.668 (20°)
2,2-Dimethylbutane	C_6H_{14}	−144.8	−98.2	121.5	49.7	0.649 (20°)
2,3-Dimethylbutane	C_6H_{14}	−211.2	−135.1	136.6	58.1	0.662 (20°)
Heptanes						
n-Heptane	C_7H_{16}	−130.9	−90.5	209.1	98.4	0.684 (20°)
Isoheptane (2-methylhexane)	C_7H_{16}	−182.4	−119.1	194	90	0.679 (20°)
3-Methylhexane	C_7H_{16}	−182.9	−119.4	197.2	91.8	0.687 (20°)
3-Ethylpentane	C_7H_{16}	−181.8	−118.8	199.9	93.3	0.698 (20°)
2,2-Dimethylpentane	C_7H_{16}	−194.1	−125.6	174	78.9	0.674 (20°)
2,3-Dimethylpentane	C_7H_{16}			193.5	89.7	0.695 (20°)
2,4-Dimethylpentane	C_7H_{16}	−182.9	−119.4	177.4	80.8	0.675 (20°)
3,3-Dimethylpentane	C_7H_{16}	−211	−135	186.8	86	0.693 (20°)
2,2,3-Trimethylbutane	C_7H_{16}	−13	−25	177.6	80.9	0.690 (20°)
Octanes						
n-Octane	C_8H_{18}	−70.4	−56.9	258.1	125.6	0.703 (20°)
Isoöctane (2-methylheptane)	C_8H_{18}	−168.3	−111.3	243	117.2	0.698 (20°)
2,2,4-Trimethylpentane[b]	C_8H_{18}	−160.3	−107.4	210.7	99.3	0.692 (20°)
n-Nonane	C_9H_{20}	−64.7	−53.7	303.3	150.7	0.718 (20°)
n-Decane	$C_{10}H_{22}$	−21.5	−29.7	345.2	174	0.730 (20°)
n-Undecane	$C_{11}H_{24}$	−14.3	−25.7	384.4	195.8	0.740 (20°)
n-Dodecane	$C_{12}H_{26}$	14.4	−9.7	420.6	216.2	0.749 (20°)
n-Tridecane	$C_{13}H_{28}$	21.2	−6	453.2	234	0.772 (0°)
n-Tetradecane	$C_{14}H_{30}$	41.9	5.5	486.5	252.5	0.774 (at m.p.)
n-Pentadecane	$C_{15}H_{32}$	50	10	518.9	270.5	0.776 (at m.p.)
n-Hexadecane (cetane)	$C_{16}H_{34}$	64.4	18	549.5	287.5	0.775 (at m.p.)
n-Heptadecane	$C_{17}H_{36}$	72.5	22.5	577.4	303	0.777 (at m.p.)
n-Octadecane	$C_{18}H_{38}$	82.4	28	602.6	317	0.777 (at m.p.)
n-Nonadecane	$C_{19}H_{40}$	89.6	32	626	330	0.777 (at m.p.)
n-Eicosane	$C_{20}H_{42}$	97.7	36.5	401	205 (15 mm.)	0.778 (at m.p.)
n-Heneicosane	$C_{21}H_{44}$	104.9	40.5	419	215 (15 mm.)	0.778 (at m.p.)
n-Docosane	$C_{22}H_{46}$	111.9	44.4	436.1	224.5 (15 mm.)	0.778 (at m.p.)
n-Tricosane	$C_{23}H_{48}$	117.8	47.7	453.2	234 (15 mm.)	0.778 (at m.p.)
n-Tetracosane	$C_{24}H_{50}$	123.8	51	615.2	324	0.779 (at m.p.)
n-Pentacosane	$C_{25}H_{52}$	129.2	54	761	405	0.779 (20°)
n-Hexacosane	$C_{26}H_{54}$	134.6	57	784.4	418	0.779 (20°)
n-Heptacosane	$C_{27}H_{56}$	139.1	59.5	518	270 (15 mm.)	0.780 (at m.p.)

[a] At 760 mm. mercury unless otherwise specified.
[b] This chemical used as standard in octane rating.

Source: (18)

From CHEMICAL REFINING OF PETROLEUM by
Vladimir Kalichevsky c. 1942 by Litton
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Reinhold Company

Table 14

Some Typical Paraffinic Hydrocarbons (cont.)

	Formula	Melting Point (°F.)	Melting Point (°C.)	Boiling Point* (°F.)	Boiling Point* (°C.)	Sp. Gr. at °C.
n-Octacosane	$C_{28}H_{58}$	143.6	62	834.8	446	0.779 (20°)
n-Nonacosane	$C_{29}H_{60}$	146.3	63.5	896	480	0.780 (20°)
n-Triacontane	$C_{30}H_{62}$	150.8	66	861.8	461	0.780 (20°)
n-Hentriacontane	$C_{31}H_{64}$	154.6	68.1	575.6	302 (15 mm.)	0.781 (at m.p.)
n-Dotriacontane (dicetyl)	$C_{32}H_{66}$	158	70	590	310 (15 mm.)	0.773 (80°)
n-Tritriacontane	$C_{33}H_{68}$	161.6	72	622.4	328 (15 mm.)	0.780 (at m.p.)
n-Tetratriacontane	$C_{34}H_{70}$	163.4	73	908.6	487	0.780 (at m.p.)
n-Pentatriacontane	$C_{35}H_{72}$	166.5	74.7	627.8	331 (15 mm.)	0.782 (at m.p.)
n-Hexatriacontane	$C_{36}H_{74}$	168.8	76	509	265 (1.0 mm.)	0.782 (at m.p.)
n-Tetracontane	$C_{40}H_{82}$	177.8	81	465.8	241 (0.3 mm.)	
n-Pentacontane	$C_{50}H_{102}$	199.4	93	789.8	421 (15 mm.)	0.794 (at m.p.)
n-Hexacontane	$C_{60}H_{122}$	210.2	99			
n-Dohexacontane	$C_{62}H_{126}$	213.8	101			
n-Tetrahexacontane	$C_{64}H_{130}$	215.6	102			
n-Heptacontane	$C_{70}H_{142}$	221	105			

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Table 15

Some Typical Naphthenic Hydrocarbons

Name	Formula		Melting Point (°F.)	Melting Point (°C.)	Boiling Point at 760 mm. (°F.)	Boiling Point at 760 mm. (°C.)	Sp. Gr. at °C.
Cyclopropane	C_3H_6	C_3H_6	−195.9	−126.6	−29.9	−34.4	0.720 (−79°)
Methylcyclopropane	C_4H_8	$CH_3 \cdot C_3H_5$			41	5	0.691 (−20°)
1,1-Dimethylcyclopropane	C_5H_{10}	$(CH_3)_2 \cdot C_3H_4$			69.8	21	0.660 (20°)
1,1,2-Trimethylcyclopropane	C_6H_{12}	$(CH_3)_3 \cdot C_3H_3$			127	52.8	0.695 (20°)
1,2,3-Trimethylcyclopropane	C_6H_{12}	$(CH_3)_3 \cdot C_3H_3$			149	65	0.692 (22°)
Cyclobutane	C_4H_8	C_4H_8	−58	−50	55.4	13	0.703 (0°)
Methylcyclobutane	C_5H_{10}	$CH_3 \cdot C_4H_7$			107.6	42	0.694 (20°)
Ethylcyclobutane	C_6H_{12}	$C_2H_5 \cdot C_4H_7$			161.6	72	0.745 (20°)
3-Cyclobutylpentane	C_9H_{18}	$C_4H_7 \cdot CH(C_2H_5) \cdot C_2H_5$			303.8–309.2	151	0.795 (19°)
Cyclopentane	C_5H_{10}	C_5H_{10}	−135.9	−93.3	122	50	0.751 (20°)
Methylcyclopentane	C_6H_{12}	$CH_3 \cdot C_5H_9$	−220.9	−140.5	161.6	72	0.750 (20°)
1,1-Dimethylcyclopentane	C_7H_{14}	$(CH_3)_2 \cdot C_5H_8$			189.5	87.5	0.755 (20°)
1,2-Dimethylcyclopentane	C_7H_{14}	$(CH_3)_2 \cdot C_5H_8$			197.6	92	0.753 (20°)
1,3-Dimethylcyclopentane	C_7H_{14}	$(CH_3)_2 \cdot C_5H_8$			195.8	91	0.754 (20°)
1-Methyl-2-ethylcyclopentane	C_8H_{16}	$(CH_3)(C_2H_5) \cdot C_5H_8$			255.2	124	
1-Methyl-3-ethylcyclopentane	C_8H_{16}	$(CH_3)(C_2H_5) \cdot C_5H_8$			249.8	121	0.764 (20°)
Cyclohexane	C_6H_{12}	C_6H_{12}	43.7	6.5	178.5	81.4	0.779 (20°)
Methylcyclohexane	C_7H_{14}	$CH_3 \cdot C_6H_{11}$	−195.3	−126.3	213.4	100.8	0.770 (20°)
1,1-Dimethylcyclohexane	C_8H_{16}	$(CH_3)_2 \cdot C_6H_{10}$	−71.5	−57.5	248	120	0.779 (20°)
1,2-Dimethylcyclohexane	C_8H_{16}	$(CH_3)_2 \cdot C_6H_{10}$			254.2	124	0.771 (20°)
1,3-Dimethylcyclohexane	C_8H_{16}	$(CH_3)_2 \cdot C_6H_{10}$	−122.8	−86	249.8	120.5	0.769 (20°)
1,4-Dimethylcyclohexane	C_8H_{16}	$(CH_3)_2 \cdot C_6H_{10}$			248	120	0.766 (20°)
Ethylcyclohexane	C_8H_{16}	$C_2H_5 \cdot C_6H_{11}$			266	130	0.777 (20°)
1,1,3-Trimethylcyclohexane	C_9H_{18}	$(CH_3)_3 \cdot C_6H_9$			280.4	138	0.790 (20°)
1,2,4-Trimethylcyclohexane	C_9H_{18}	$(CH_3)_3 \cdot C_6H_9$			284 −287.6	140–2	0.778 (20°)
1,3,5-Trimethylcyclohexane	C_9H_{18}	$(CH_3)_3 \cdot C_6H_9$			278.6–282.2	137–9	0.772 (20°)
1-Methyl-2-ethylcyclohexane	C_9H_{18}	$(CH_3)(C_2H_5) \cdot C_6H_{10}$			303.8	151	0.784 (20°)
1-Methyl-3-ethylcyclohexane	C_9H_{18}	$(CH_3)(C_2H_5) \cdot C_6H_{10}$			300.2	149	0.799 (20°)
1-Methyl-4-ethylcyclohexane	C_9H_{18}	$(CH_3)(C_2H_5) \cdot C_6H_{10}$			302	150	0.804 (0°)
Propylcyclohexane	C_9H_{18}	$C_3H_7 \cdot C_6H_{11}$			301.1	149.5	0.767 (20°)
Isopropylcyclohexane	C_9H_{18}	$C_3H_7 \cdot C_6H_{11}$			302	150	0.787 (20°)
1-Methyl-4-isopropylcyclohexane	$C_{10}H_{20}$	$(CH_3)(C_3H_7) \cdot C_6H_{10}$			336.2–338	169–70	0.793 (20°)
1,3-Diethylcyclohexane	$C_{10}H_{20}$	$(C_2H_5)_2 \cdot C_6H_{10}$			336.2–339.8	169–71	0.796 (22°)
Cycloheptane	C_7H_{14}	C_7H_{14}	10.4	−12	244.6	118.1	0.811 (20°)
Ethylcycloheptane	C_9H_{18}	$C_2H_5 \cdot C_7H_{13}$	<−22	<−30	390.2	199	0.952 (20°)
Cyclooctane	C_8H_{16}	C_8H_{16}	57.7	14.3	298.4–300.2	148–9	0.835 (20°)
Cyclononane	C_9H_{18}	C_9H_{18}			341.6	172	0.773 (16°)

Source: (18)

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Table 16

Some Typical Aromatic Hydrocarbons

Name	Formula		Melting Point (°F.)	Melting Point (°C.)	Boiling Point at 760 mm. (°F.)	Boiling Point at 760 mm. (°C.)	Sp. Gr. at °C.
Benzene	C_6H_6	C_6H_6	41.9	5.5	176	80	0.878 (20°)
Toluene	C_7H_8	$C_6H_5 \cdot CH_3$	−139.2	−95.1	231.1	110.6	0.867 (20°)
Xylenes, dimethylbenzenes							
o-xylene	C_8H_{10}	$C_6H_4 \cdot (CH_3)_2$	−16.6	−27	291.2	144	0.879 (20°)
m-xylene	C_8H_{10}	$C_6H_4 \cdot (CH_3)_2$	−53.3	−47.4	282.6	139	0.864 (20°)
p-xylene	C_8H_{10}	$C_6H_4 \cdot (CH_3)_2$	55.8	13.2	281.1	138.4	0.861 (20°)
Ethylbenzene	C_8H_{10}	$C_6H_5 \cdot C_2H_5$	−137.2	−94	277	136.1	0.867 (20°)
Trimethylbenzenes							
1,2,3-trimethylbenzene	C_9H_{12}	$C_6H_3 \cdot (CH_3)_3$	−13.9	−25.5	349.7	176.1	0.895 (20°)
1,2,4-trimethylbenzene	C_9H_{12}	$C_6H_3 \cdot (CH_3)_3$	−49	−45	336.6	169.2	0.876 (20°)
1,3,5-trimethylbenzene	C_9H_{12}	$C_6H_3 \cdot (CH_3)_3$	−61.1	−51.7	328.3	164.6	0.863 (20°)
Methylethylbenzenes							
1-methyl-2-ethylbenzene (*o*-ethyltoluene)	C_9H_{12}	$C_6H_4 \cdot (CH_3)(C_2H_5)$			329	165	0.882 (20°)
1-methyl-3-ethylbenzene (*m*-ethyltoluene)	C_9H_{12}	$C_6H_4 \cdot (CH_3)(C_2H_5)$			323.6	162	0.867 (20°)
1-methyl-4-ethylbenzene (*p*-ethyltoluene)	C_9H_{12}	$C_6H_4 \cdot (CH_3)(C_2H_5)$	< -4	< -20	323.6	162	0.862 (20°)
n-Propylbenzene	C_9H_{12}	$C_6H_5 \cdot C_3H_7$	−150.9	−101.6	318.2	159	0.862 (20°)
Isopropylbenzene (cumene)	C_9H_{12}	$C_6H_5 \cdot CH(CH_3)_2$	−142.4	−96.9	307.4	153	0.862 (20°)
Tetramethylbenzenes							
1,2,3,4-tetramethylbenzene	$C_{10}H_{14}$	$C_6H_2 \cdot (CH_3)_4$	24.8	−4	399.2	204	0.901 (20°)
1,2,3,5-tetramethylbenzene	$C_{10}H_{14}$	$C_6H_2 \cdot (CH_3)_4$	−11.2	−24	384.8	196	0.896 (0°)
1,2,4,5-tetramethylbenzene	$C_{10}H_{14}$	$C_6H_2 \cdot (CH_3)_4$	176	80	381.2	194	0.838 (81.3°)
Methylisopropylbenzenes							
1-methyl-2-isopropylbenzene	$C_{10}H_{14}$	$C_6H_4 \cdot (CH_3)(C_3H_7)$			350.6	177	0.876 (20°)
1-methyl-3-isopropylbenzene	$C_{10}H_{14}$	$C_6H_4 \cdot (CH_3)(C_3H_7)$	> -13	> -25	347	175	0.860 (20°)
1-methyl-4-isopropylbenzene	$C_{10}H_{14}$	$C_6H_4 \cdot (CH_3)(C_3H_7)$	−100.3	−73.5	350.6	177	0.857 (20°)
Pentamethylbenzene	$C_{11}H_{16}$	$C_6H \cdot (CH_3)_5$	127.4	53	446	230	0.853 (100°)
Hexamethylbenzene	$C_{12}H_{18}$	$C_6 \cdot (CH_3)_6$	330.8	166	509	265	
Pentaethylbenzene	$C_{16}H_{26}$	$C_6H \cdot (C_2H_5)_5$	< -4	< -20	530.6	277	0.896 (20°)
Hexaethylbenzene	$C_{18}H_{30}$	$C_6 \cdot (C_2H_5)_6$	258.8	126	568.4	298	0.830 (130°)

Source: (18)

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Table 17

Some Hydrocarbons in a Mid-Continent Crude Oil

No.	Formula	Name and Type of Hydrocarbon	Boiling Point at 1 Atm. °C.	Purity of Best Sample Isolated (Mol Per Cent)	Estimated Relative Amount by Volume [a]
		Paraffinic			
1	CH_4	Methane	−161.7	[b]	[b]
2	C_2H_6	Ethane	− 88.6	[b]	[b]
3	C_3H_8	Propane	− 42.2	[b]	[b]
4	C_4H_{10}	*Iso*butane	− 12.1	[b]	[b]
5	C_4H_{10}	*n*-Butane	− 0.5	[b]	[b]
6	C_5H_{12}	2-Methylbutane	27.9	[b]	[b]
7	C_5H_{12}	*n*-Pentane	36.1	[b]	[b]
8	C_6H_{14}	2,3-Dimethylbutane	58.0	>95	0.06
9	C_6H_{14}	2-Methylpentane	60.3	>95	0.1
10	C_6H_{14}	3-Methylpentane	63.3	>95	0.2
11	C_6H_{14}	*n*-Hexane	68.7	98.3	0.7
12	C_7H_{16}	2,2-Dimethylpentane	78.9	54	0.04
13	C_7H_{16}	2-Methylhexane	90.0	99.9	0.3
14	C_7H_{16}	3-Methylhexane	91.8	[c]	0.2
15	C_7H_{16}	*n*-Heptane	98.4	>99.8	1.1
16	C_8H_{18}	2-Methylheptane	117.2	97	0.5
17	C_8H_{18}	*n*-Octane	125.6	99.1	1.0
18	C_9H_{20}	2,6-Dimethylheptane	135.2	>99	0.1
19	C_9H_{20}	*Iso*nonane	140.8	85	0.05
20	C_9H_{20}	4-Methyloctane	142.4	80	0.06
21	C_9H_{20}	2-Methyloctane	143.3	99.9	0.2
22	C_9H_{20}	3-Methyloctane	144.2	95	0.06
23	C_9H_{20}	*n*-Nonane	150.7	99.9	1.0
24	$C_{10}H_{22}$	*n*-Decane	174.0	>99.99	0.8
		Naphthenic			
25	C_5H_{10}	Cyclopentane	49.5	[b]	[b]
26	C_6H_{12}	Methylcyclopentane	71.9	98.7	0.2
27	C_6H_{12}	Cyclohexane	80.8	99.96	0.3
28	C_7H_{14}	1,1-Dimethylcyclopentane	87.5	95	0.05
29	C_7H_{14}	Methylcyclohexane	100.8	>99.8	0.3
30	C_8H_{16}	Octanaphthene	119.8	[b]	0.2
31	C_8H_{16}	1,3-Dimethylcyclohexane	120.3	98	
32	C_8H_{16}	Octanaphthene (1,2-dimethylcyclohexane?)	123.4	91	0.04
33	C_8H_{16}	Ethylcyclohexane	131.8	95	0.1
34	C_9H_{18}	Nonanaphthene (alkyl cyclopentane)	136.7	>99	0.1
35	C_9H_{18}	Nonanaphthene	141.2	95	0.08
		Aromatic			
36	C_6H_6	Benzene	80.1	99.8	0.08
37	C_7H_8	Toluene	110.6	[b]	0.3
38	C_8H_{10}	Ethylbenzene	136.2	95	0.03
39	C_8H_{10}	*p*-Xylene	138.4	>99.9	0.04
40	C_8H_{10}	*m*-Xylene	139.2	>99.9	0.1
41	C_8H_{10}	*o*-Xylene	144.4	>99	0.1
42	C_9H_{12}	*Iso*propylbenzene	152.4	98.4	0.03
43	C_9H_{12}	1,3,5-Trimethylbenzene (mesitylene)	164.6	99.95	0.02
44	C_9H_{12}	1,2,4-Trimethylbenzene (pseudocumene)	169.2	99.9	0.2
45	C_9H_{12}	1,2,3-Trimethylbenzene (hemimellitene)	176.1	99.95	0.06

[a] The numbers in this column give the estimated relative amounts by volume of the given hydrocarbon in the petroleum, referred to normal octane or normal nonane (which are present in substantially equal amounts) as unity. In order to obtain the order of magnitude of the *percentage content* of the given hydrocarbon in the original crude, these figures should be multiplied by a factor which is roughly estimated to be somewhere between 1 and 1.66

[b] Not determined.

[c] Determination not yet completed.

Source: (18)

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By molecular type:

paraffin hydrocarbons (alkanes)	30%
naphthene hydrocarbons (cycloalkanes)	50%
aromatic hydrocarbons	15%
nitrogen, sulfur and oxygen - containing compounds	5%

By molecular size:

$C_5 - C_{10}$	(gasoline)	30%
$C_{10} - C_{12}$	(kerosene)	10%
$C_{12} - C_{20}$	(light distillate oil)	15%
$C_{20} - C_{40}$	(heavy distillate oil)	25%
$>C_{40}$	(residual oil)	20%

Any specific crude may differ appreciably from these average values. For example, Lagomedio crude oil from Venezuela would contain about 10 percent paraffins (alkanes), 45 percent naphthenes (cycloalkanes), 25 percent aromatics and 20 percent nitrogen, sulfur and oxygen-containing compounds. In contrast a south Texas crude has a larger percentage of smaller molecular sizes and a greater amount of paraffin-naphthene hydrocarbons than the worldwide crude average.

Crude oils can be divided roughly into three main groups on the basis of hydrocarbon structural predominance; paraffinic, naphthenic, and aromatic. Paraffinic (alkanic) crude oils contain mostly saturated straight and branch chained carbon compounds, along with lesser amounts of cycloalkanes and aromatics. They include the lightest of all crudes. Most of the crudes used by the Puget Sound refineries are paraffinic crudes. Naphthenic crudes, also called cycloparaffins, contain appreciable quantities of compounds with at least one saturated ring structure and bear a close resemblance to paraffinic crudes. The aromatic crude oils generally are heavier, with higher boiling points and contain a large concentration of unsaturated benzene ring structures. Aromatic crudes also usually contain a high sulfur content (two percent or more).

The crude oils which have been utilized by the Puget Sound refineries during the past three years and those which may be used to replace the diminishing supply of Canadian crudes also can be categorized, according to the occurrence of these three classes of hydrocarbons, as being paraffinic, naphthenic or aromatic crudes (Tables 18 and 19). In some instances, however, there is no clear predominance of one class of hydrocarbons over the others. Arabian Light crude oil, for example, is largely naphthenic,

Table 18

General Chemical Classification of Crude Oils Received from 1974-1976 by Puget Sound Refineries

Crude Oil	Predominant Chemical Characteristis		
	Paraffinic	Naphthenic	Aromatic
Arabian Light		●	●
Berri		●	
Iranian Light		●	●
Iranian Heavy		●	●
Sassan		●	●
Murban	●		
Attaka	●		●
Minas	●		
Arjuna	●		●
Walio Export Mix	●		
Bekapi	●		
Poleng	●		
Labuan Light	●		●
Lagomedio	●	●	
Oriente	●		
Brass River	●		
Qua Iboe	●		
Bonny Light	●		
Canadian	●		
Cook Inlet	●		
San Ardo		●	●
San Joaquin		●	
Santa Maria		●	

Table 19

General Chemical Classification of Crude Oils Under Consideration by Puget Sound Refineries for Replacement of Canadian Crude Oils

Crude Oil	Predominant Chemical Characteristic		
	Paraffinic	Naphthenic	Aromatic
Qua Iboe	●		
Forcados	●		
Brass River	●		
Bonny Light	●		
Escravos	●		
Pennington	●		
Zuetina	●		
Es Sider	●		
Bu Attifel	●		
Brega	●		
Sarir	●		
Amna	●		
Oriente	●		
Lagomedio	●	●	
Arjuna	●		●
Attaka	●		●
Bekapai	●		
Cinta	●		
Labuan Light	●		●
Minas	●		
Poleng	●		
Badak	●		
Sepinggan	●		
Bunju	●		
Handil	●		
Arzew	●		
Zarzaitine	●		
Hassi Messaoud	●		

Table 19 (cont.)

General Chemical Classification of Crude Oils Under Consideration by Puget Sound Refineries for Replacement of Canadian Crude Oils

Crude Oil	Predominant Chemical Characteristic		
	Paraffinic	Naphthenic	Aromatic
Gamba	●		
Anguille	●		
Cabinda	●		
Murban	●		
Cook Inlet	●		
North Slope	●	●	

but also has a fairly high aromatic content. For these cases, more than one category is noted in Tables 18 and 19.

Petroleum in its various types and fractions has been observed to cause mortality among marine organisms. The manner in which crude oils and petroleum products can affect marine life is (1) directly -- by chemical, physiological or mechanical means, or (2) indirectly -- by oxygen reduction, carbon dioxide concentrations or accumulative synergistic effects. The chemical toxicity of a crude oil to marine life varies according to the classification to which it belongs, the volatility of the hydrocarbons present, and its solubility in seawater. Toxicity is a function of reactivity; the more reactive a compound, the more likely it will interfere with biological functions. Paraffinic compounds do not tend to mix easily with water or biological tissues, and do not tend to react biologically. Therefore, the toxicity of these compounds is almost always low. Highly substituted compounds can react more easily, and their toxicities cover a wide range depending on the nature of the substitutions. Aromatic compounds are very reactive in biological systems, and have high toxicities. So crude oils classed as aromatic, containing a predominance of aromatic compounds, are generally more toxic than the light, waxy crudes. Even naphthenic crudes, which contain saturated cyclic compounds are less toxic because these ring compounds are more easily degraded than are the aromatic unsaturated benzene rings. Also the higher sulfur content frequently associated with aromatic crudes increases the initial toxicity because it tends to inhibit oxidative processes, allowing the more volatile fractions to remain unoxidized in sea water.

The volatility of the hydrocarbon compounds appears to be another factor influencing toxicity. Small, low-boiling molecules, especially the more reactive hydrocarbons, can easily penetrate biological tissues and are very damaging in terms of toxicity. Therefore, volatile hydrocarbons are generally more harmful than nonvolatile compounds in the same hydrocarbon class. Consequently some volatile aromatics are considered to be the most toxic types of hydrocarbons, although other low-boiling, non-aromatic hydrocarbons may also be highly toxic. Defining which compounds are volatile and which are nonvolatile has been a subject of controversy in the past. A compromise classification method defines those hydrocarbons with boiling points of less than 457°F (236°C) as volatiles. This includes all hydrocarbons through C_{13}. All hydrocarbons above C_{13} have boiling points above 457°F and are classed as nonvolatiles. The relative general occurrence of volatiles and nonvolatiles in crude oils is shown in Table 20. Tables 21 and 22 present the relative percentages of volatile compounds that occur in crudes used by Puget Sound refineries and those crude oils which may replace the dwindling supply of Canadian crudes. Whenever possible the breakdown of volatiles to specific hydrocarbon classes has been indicated.

The actual effect of these potentially toxic volatile compounds on marine organisms is generally reduced by the physical weathering processes that exert their influence as soon as the crude oil enters the marine environment. The volatile hydrocarbons evaporate fairly rapidly under most conditions. Evaporation is greatly enhanced by wind and wave action, and is most intense during the first week after the oil enters the water.

Table 20

Relative Quantity of Volatiles and Nonvolatiles in Crude Oils

Class	Boiling Point (°F)	Carbon Number	Volume Percent
Volatiles	<457	$C_1 - C_{13}$	20 - 50
Nonvolatiles	457-968	$C_{14} - C_{40}$	35 - 50
	<968	$C_{41}+$	7 - 45

Source: (12)

Table 21

Relative Percentages of Volatiles (Total and by Hydrocarbon Class) in Crude Oils Received from 1974-1976 by Puget Sound Refineries

Crude Oil	Total Volatiles	Volatile Aromatics	Volatile Naphthenes	Volatile Paraffins
Arabian Light	35	4	7	24
Berri	38	5	7	26
Iranian Light	34	6	11	17
Iranian Heavy	32	5	11	16
Sassan	35	7	11	17
Murban	41	7	8	26
Attaka	61	16	9	36
Minas	23	2	7	14
Arjuna	36	8	12	16
Walio Export Mix	39	2	14	23
Bekapai	41	--	--	--
Poleng	60	11	22	27
Labuan Light	43	9	14	20
Lagomedio	30	--	--	--
Oriente	30	4	12	14
Brass River	54	7	27	20
Qua Iboe	42	5	22	15
Bonny Light	36	4	17	15
Canadian	35-44	--	--	--
Cook Inlet	37-47	--	--	--
San Ardo	--	--	--	--
San Joaquin	--	--	--	--
Santa Maria	--	--	--	--

Table 22

Relative Percentage of Volatiles (Total and by Hydrocarbon Class) in Crude Oils Under Consideration by Puget Sound Refineries for Replacement of Canadian Crude Oils

Crude Oil	Total Volatiles	Volatile Aromatics	Volatile Naphthenes	Volatile Paraffins
Qua Iboe	42	5	22	15
Forcados	27	3	13	11
Brass River	54	7	27	20
Bonny Light	36	4	17	15
Escravos	37	6	15	16
Pennington	39	4	20	15
Zuetina	33	4	11	18
Es Sider	34	4	9	21
Bu Attifel	25	2	4	19
Brega	41	5	12	24
Sarir	26	1	10	15
Amna	27	1	8	18
Oriente	30	4	12	14
Lagomedio	30	--	--	--
Arjuna	36	8	12	16
Attaka	61	16	9	36
Bekapai	41	--	--	--
Cinta	--	--	--	--
Labuan Light	43	9	14	20
Minas	23	2	7	14
Poleng	60	11	22	27

Table 22 (cont.)

Crude Oil	Total Volatiles	Volatile Aromatics	Volatile Naphthenes	Volatile Paraffins
Badak	--	--	--	--
Sepinggan	47	11	--	--
Bunju	44	--	--	--
Handil	24	10	--	--
Arzew	42	3	9	30
Zarzaitine	37	6	12	19
Hassi Messaoud	47	6	14	27
Gamba	15	--	--	--
Anguille	27	2	9	16
Cabinda	25	3	7	15
Murban	41	7	8	26
Cook Inlet	37-47	--	--	--
North Slope	26	4	9	13

Figure 6 shows the decrease of the volatile fractions and the relative stability of the nonvolatile hydrocarbons during artifical laboratory weathering of a Kuwait crude oil. Generally, even the most intense weathering action only affects hydrocarbons with boiling points below 350°C. Thus the effect of these volatile hydrocarbons on marine organisms will vary, depending on the type of volatile hydrocarbon (the aromatics being the most toxic) present and the rate and degree of weathering, causing these hydrocarbons to evaporate from the marine environment.

The water solubilities of the hydrocarbon compounds also will effect the toxicity of a given crude oil. For a specific class of hydrocarbons, the solubility in water decreases as the molecular weight increases. For the classes of hydrocarbons, solubility increases from alkanes to cycloalkanes to aromatics. Some solubility values for the various classes of hydrocarbons are shown below.

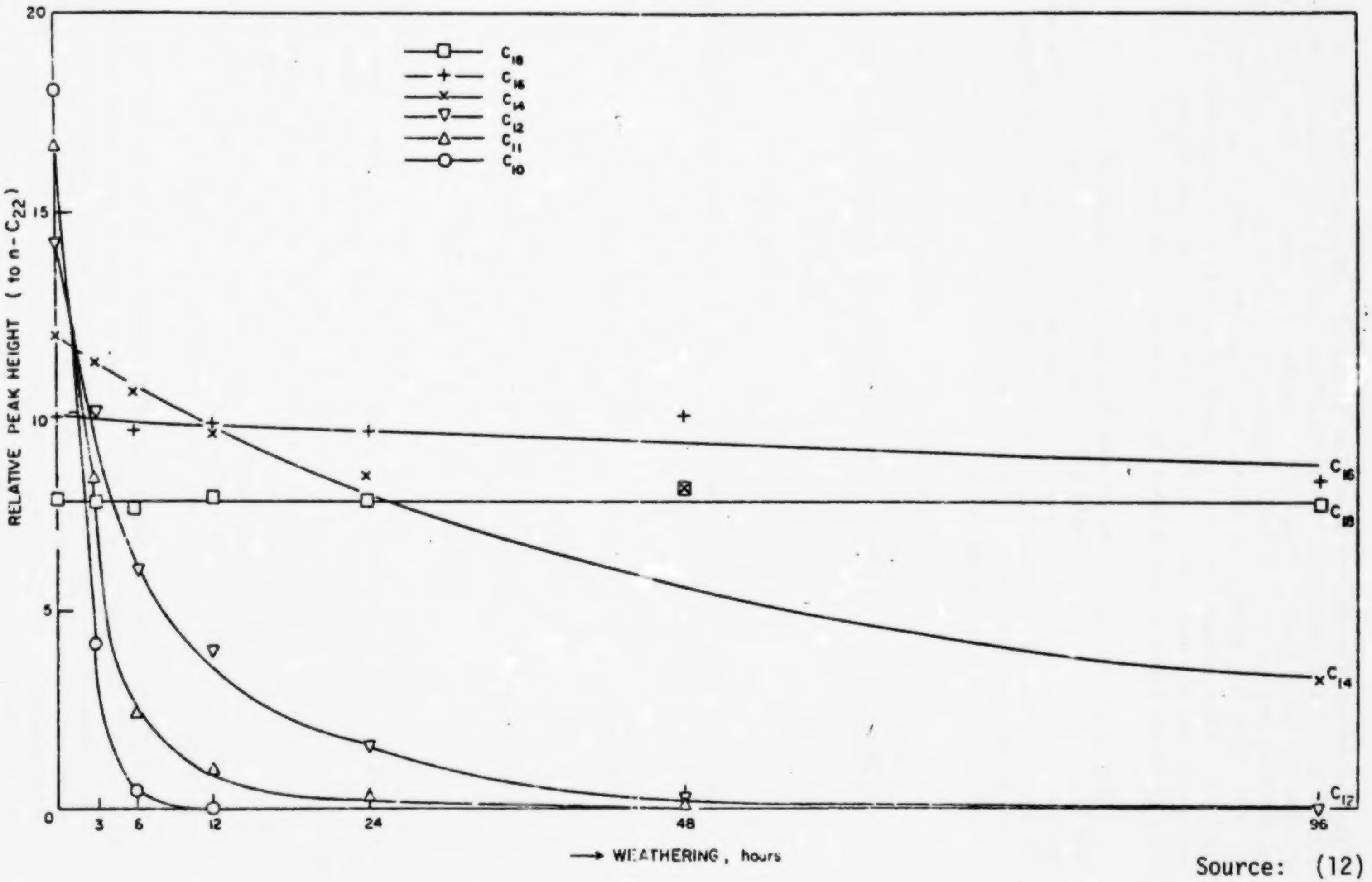
Class of Hydrocarbon	Hydrocarbon of Class with Highest Solubility in Water	Solubility of a Higher Molecular Weight Hydrocarbon in Class
Alkanes	Ethane	Decane
	42 ppm	0.035 ppm
Cycloalkanes	Cyclopentane	1,2-Dimethylcyclohexane
		4.2 ppm
Olefins	Propene	1-Octene
	140 ppm	2.1 ppm
Aromatics	Benzene	Isopropylbenzene
	1246 ppm	35 ppm

These values are for sea water. In freshwater the solubility would be somewhat greater. Crude oils in equilibrium with sea water typically have from 10-30 ppm total dissolved hydrocarbons, of which about half may be low molecular weight aromatic hydrocarbons. Thus the low molecular weight, volatile aromatic hydrocarbons are not only the most toxic hydrocarbons, they are the most soluble in water. The actual extent to which these soluble hydrocarbons affect marine organisms will depend on the quantity in a specific crude and the length of time required to reduce these hydrocarbons by weathering and other degradative processes.

To further identify the effects of crude oils on the marine environment, it will be necessary in the future to have a much more detailed hydrocarbon breakdown for each crude. Identification of specific compounds will allow application of solubilities to determine which toxic hydrocarbons could potentially be mixed with the marine waters. Until then, classification according to specific hydrocarbon types and examination of the percentage of volatile compounds must suffice for characterizing crude oils

Figure 6

The Effects of Artificial Weathering of the Volatile and Nonvolatile Hydrocarbons in a Kuwait Crude Oil



Source: (12)

as to their relative toxicities to the marine environment. On this basis, a tentative subjective rating of the crude oils being used by the Puget Sound refineries indicates that the following crudes are the most harmful to marine organisms: Attaka, Poleng, Labuan Light, Arjuna, Brass River, Sassan and Murban. Other crudes which would be expected to have very harmful effects are: Arabian Light, Iranian Light, Iranian Heavy, San Ardo and possibly San Joaquin, Santa Maria and Lagomedio. It is difficult without more detailed crude assays to distinguish and rank the remaining crudes and potential future crudes; however, they too will have toxic effects on the marine environment.

Beyond the general lethal and sub-lethal toxic effects, crude oils can also disrupt the marine ecosystem by (1) direct coating of organisms with crude; (2) tainting and/or accumulation of hydrocarbons in the food chain through incorporation of hydrocarbons in organisms, and (3) causing drastic changes in the habitats or marine organisms. These effects would be possible for all of the crude oils brought to the Puget Sound refineries. The effects of oil on a number of species have been analyzed; selected species are shown in Table 23. Biological communities damaged by oil can eventually recover naturally. However, the rate of recovery will depend on the species, the season of exposure, the type and amount of crude oil, and the frequency of exposure.

C. Refined Products Utilized or Produced in Puget Sound

1. Introduction

The production of refined products is directly related to the type of crude oils being used, the design of the refinery and the relative amounts of each product the refinery management desires. Usually a refinery is built to utilize specific types of crude oils (light, heavy, waxy, aromatic, low sulfur, etc.), employing specific processes to yield specific types of products. The four major refineries were designed to produce a large array of fuel products, but predominantly motor gasoline and jet fuels. Mobil, Shell and Texaco were designed to utilize light, sweet (low sulfur) crudes, while ARCO employs a few additional processes to allow handling of heavier, high sulfur crudes (specifically Alaskan North Slope crudes when they become available). U.S. Oil & Refining is a smaller operation and not only produces a variety of fuels, but also was designed to process heavy asphaltic crudes to yield petroleum asphalt. Sound Refining is a very small operation and at the present is strictly capable of handling the production of asphalt, some lubricating oils, and fuel oils.

The output of the refineries varies seasonally, and to a lesser extent, monthly, in response to market demands. The local market has the highest priority, followed by market demands in Oregon and California. In general there is a seasonal shift from motor fuels in spring and summer to domestic heating oils in fall and winter. This shift is not to the exclusion of the other products; rather, it is a shifting in emphasis to accommodate the changing demand for heating oils. Sound Refining has a special problem in that the market for asphalt drops drastically in winter and the

Table 23

The Effects of Crude Oil on Selected Species

Species	Common name	Lethal	Sublethal	Coating	Uptake and tainting	Habitat change
Birds						
Rissa tridactyla	Kittiwake	-		X		
Fishes						
Alosa spp.	Alewife	X				
Clupea harengus	Herring	X				
Fundulus heteroclitus	Mummichog	X				
Gadus morhua	Atlantic cod	X				
Micropogon undulatus	Croaker		X			
Morona saxatilis	Striped bass		X			
Pseudopleuronectes americanus	Winter flounder	X	X			
Crustaceans						
Acartia spp.	Zooplankter	X				
Ampelisca vadorum	Amphipod	X				X
Balanus balanoides	Acorn barnacle	X				
Calanus spp.	Zooplankter	X			X	
Crangon spp.	Shrimp	X				
Emerita spp.	Mole crab	X				
Homarus americanus	American lobster	X	X			
Paqurus longicarpus	Hermit crab	X			X	
Pandalus spp.	Shrimp	X				
Mollusks						
Asquipecten spp.	Scallop	X	X		X	
Crassostrea spp.	Virginia oyster	X	X		X	
Donax spp.	Coquina clam	X				
Mercenaria mercenaria	Northern quahog	X				
Modiolus spp.	Horse mussel		X		X	
Mya arenia	Soft-shell clam	X			X	X
Mytilus edulis	Edible mussel	X	X	X	X	
Littorina littorea and spp.	Periwinkle	X	X	X		
Nassarius obsoletus	Common mud snail		X			
Thais lapillus	Dog wheik	X	X			
Worms						
Arenicola marina	Lugworm	X	X			X
Nereis virens	Clam worm	X				
Stroblospio benedicti	Polychaete	X				
Other animals						
Asterias vulgaris	Starfish				X	
Strongylocentrotus droebachiensis	Sea urchin	X			X	
Plants						
Juncus gerardi	Marsh rushes	X				
Spartina alterniflora	March grasses	X			X	
Spartina patens	Cord grass	X				
Laminaria spp.	Kelp	X				

[1] Does not list all species for which data have been reported. Rather, an X represents reported data for those species which were selected for special consideration. An X indicates that some data, regardless of number, have been reported.

Source: Massachusetts Institute of Technology Department of Civil Engineering, 1974, "Atlantic/Alaskan OCS Petroleum Study: Primary Biological Effects," prepared for the Council on Environmental Quality under contract No. EQC330.

Source: (14)

necessity of applying heat to move the heavy crude oil makes refinery operations relatively uneconomical in winter. So the refinery has often been shut down for five or six months of the year.

There are a number of different products that can be obtained by processing crude oils. The nominal product yield from an average barrel of oil is:

gasoline	45%
kerosene	3%
jet fuel	8%
distillate fuel oil	22%
residual fuel oil	8%
other products	14%

A more specific list of refined products available from crude oil is shown in Figure 7 and includes:

Gases (such as butane and propane)

Liquified petroleum gas (LPG)

Motor gasoline (regular, supreme, unleaded)

Aviation fuel (mainly for piston planes)

Jet fuel (JP-4, JP-5, Jet A, Jet A-1)

Kerosene

Fuel Oils

  #1 high grade diesel oil

  #2 diesel oil (six different grades)

  #3 heating oil

  #4 heating oil (for small companies, manufacturers, etc.)

  #5 heating oil (used by cities, industries, etc.)

  #6 bunker C (used by power plants, ships, heavy industries)

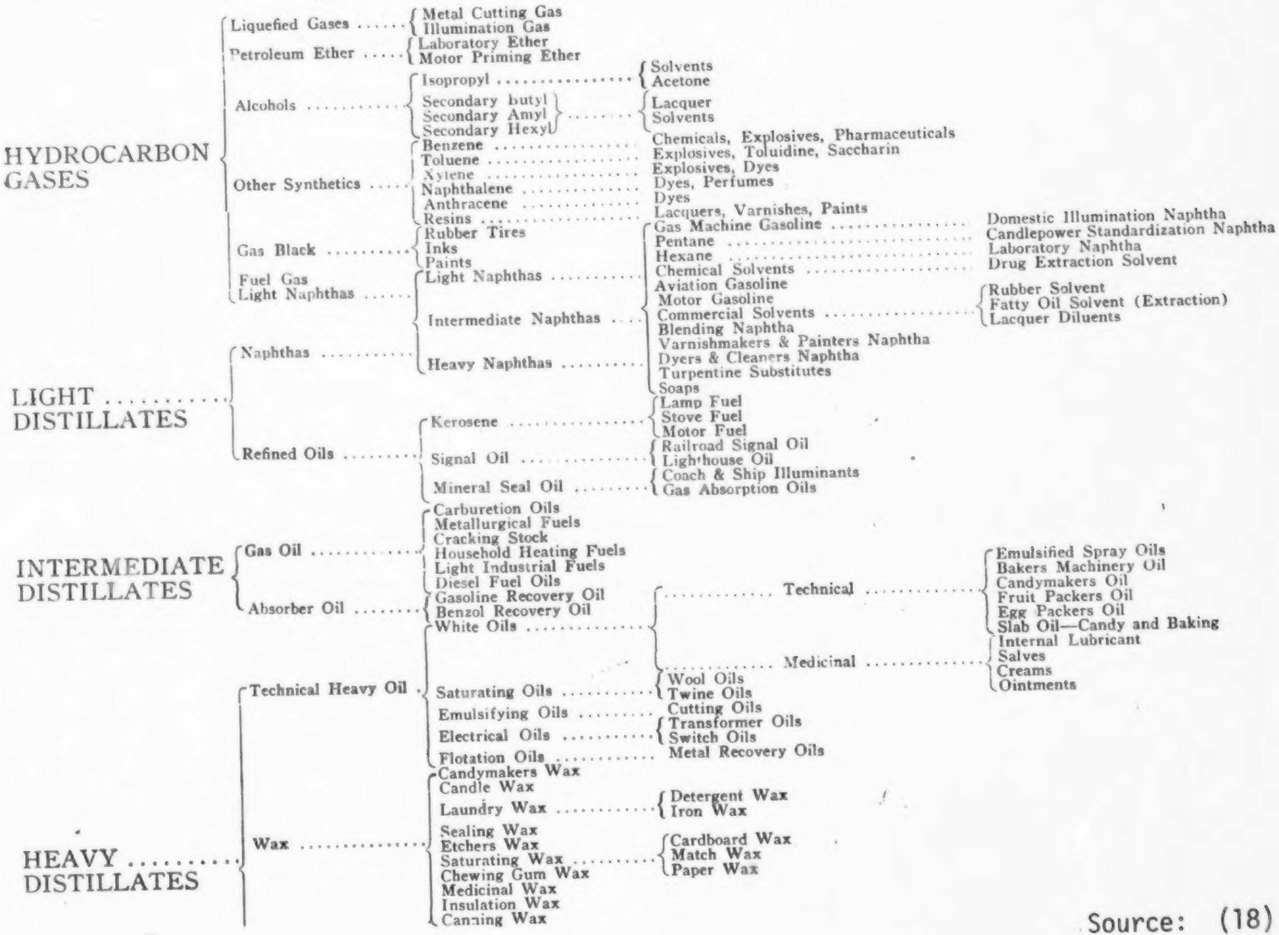
Lubricating oils, greases

Naphtha and petroleum solvents

Asphalt, tar and pitch

Figure 7

Refined Products Derived From Crude Petroleum


HYDROCARBON GASES
Liquefied Gases
Metal Cutting Gas
Illumination Gas
Petroleum Ether
Laboratory Ether
Motor Priming Ether
Alcohols
Isopropyl
Solvents
Acetone
Secondary butyl
Secondary Amyl
Secondary Hexyl
Lacquer
Solvents
Other Synthetics
Benzene
Chemicals, Explosives, Pharmaceuticals
Toluene
Explosives, Toluidine, Saccharin
Xylene
Explosives, Dyes
Naphthalene
Dyes, Perfumes
Anthracene
Dyes
Resins
Lacquers, Varnishes, Paints
Gas Black
Rubber Tires
Inks
Paints
Fuel Gas
Light Naphthas
LIGHT DISTILLATES
Naphthas
Light Naphthas
Intermediate Naphthas
Heavy Naphthas
Gas Machine Gasoline
Pentane
Hexane
Chemical Solvents
Domestic Illumination Naphtha
Candlepower Standardization Naphtha
Laboratory Naphtha
Drug Extraction Solvent
Aviation Gasoline
Motor Gasoline
Commercial Solvents
Rubber Solvent
Fatty Oil Solvent (Extraction)
Lacquer Diluents
Blending Naphtha
Varnishmakers & Painters Naphtha
Dyers & Cleaners Naphtha
Turpentine Substitutes
Soaps
Refined Oils
Kerosene
Lamp Fuel
Stove Fuel
Motor Fuel
Signal Oil
Railroad Signal Oil
Lighthouse Oil
Mineral Seal Oil
Coach & Ship Illuminants
Gas Absorption Oils
INTERMEDIATE DISTILLATES
Gas Oil
Carburetion Oils
Metallurgical Fuels
Cracking Stock
Household Heating Fuels
Light Industrial Fuels
Diesel Fuel Oils
Absorber Oil
Gasoline Recovery Oil
Benzol Recovery Oil
White Oils
Technical
Emulsified Spray Oils
Bakers Machinery Oil
Candymakers Oil
Fruit Packers Oil
Egg Packers Oil
Slab Oil—Candy and Baking
Medicinal
Internal Lubricant
Salves
Creams
Ointments
HEAVY DISTILLATES
Technical Heavy Oil
Saturating Oils
Wool Oils
Twine Oils
Emulsifying Oils
Cutting Oils
Electrical Oils
Transformer Oils
Switch Oils
Flotation Oils
Metal Recovery Oils
Wax
Candymakers Wax
Candle Wax
Laundry Wax
Detergent Wax
Iron Wax
Sealing Wax
Etchers Wax
Saturating Wax
Cardboard Wax
Match Wax
Paper Wax
Chewing Gum Wax
Medicinal Wax
Insulation Wax
Canning Wax

Source: (18)

From CHEMICAL REFINING OF PETROLEUM by Vladimir Kalichevsky
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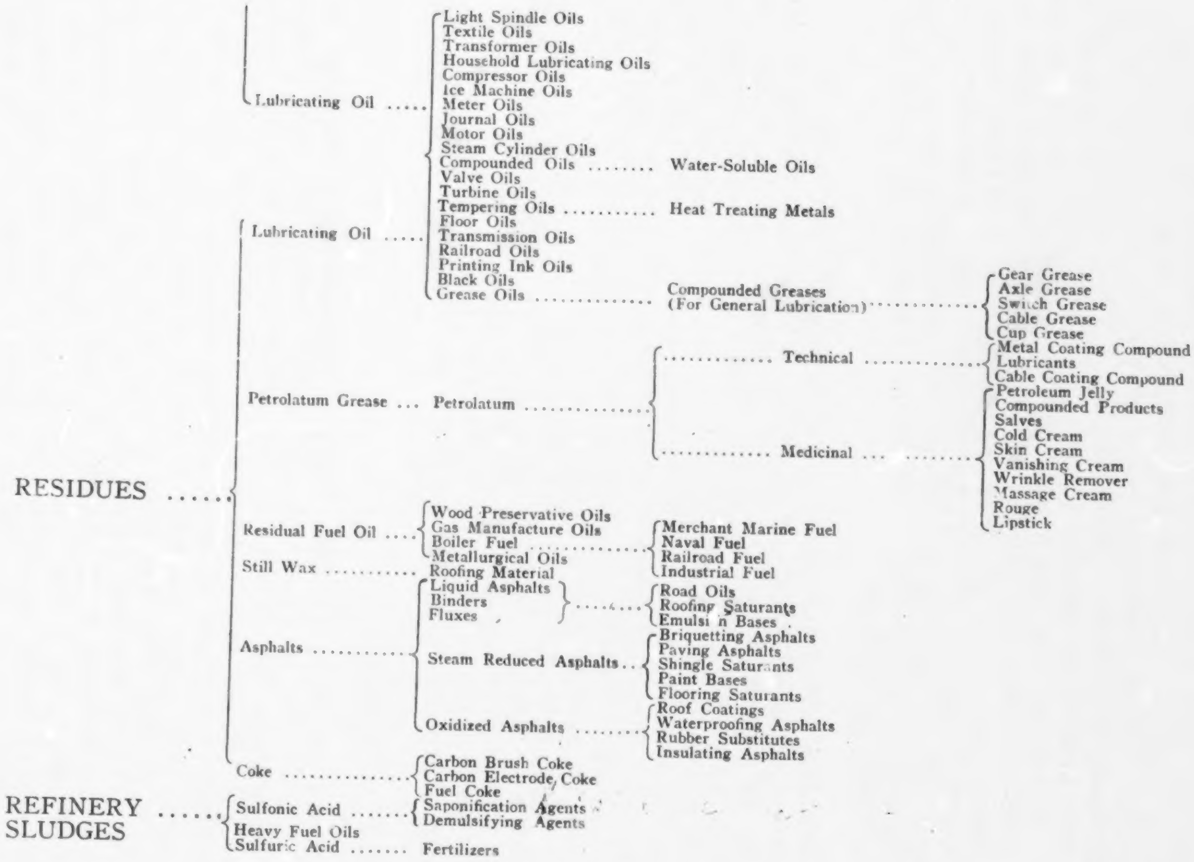
Figure 7 (cont.)



- RESIDUES
  - Lubricating Oil
  - Lubricating Oil
    - Light Spindle Oils
    - Textile Oils
    - Transformer Oils
    - Household Lubricating Oils
    - Compressor Oils
    - Ice Machine Oils
    - Meter Oils
    - Journal Oils
    - Motor Oils
    - Steam Cylinder Oils
    - Compounded Oils
      - Water-Soluble Oils
    - Valve Oils
    - Turbine Oils
    - Tempering Oils
      - Heat Treating Metals
    - Floor Oils
    - Transmission Oils
    - Railroad Oils
    - Printing Ink Oils
    - Black Oils
    - Grease Oils
      - Compounded Greases (For General Lubrication)
        - Gear Grease
        - Axle Grease
        - Switch Grease
        - Cable Grease
        - Cup Grease
  - Petrolatum Grease
    - Petrolatum
      - Technical
        - Metal Coating Compound
        - Lubricants
        - Cable Coating Compound
      - Medicinal
        - Petroleum Jelly
        - Compounded Products
        - Salves
        - Cold Cream
        - Skin Cream
        - Vanishing Cream
        - Wrinkle Remover
        - Massage Cream
        - Rouge
        - Lipstick
  - Residual Fuel Oil
    - Wood Preservative Oils
    - Gas Manufacture Oils
    - Boiler Fuel
      - Merchant Marine Fuel
      - Naval Fuel
      - Railroad Fuel
      - Industrial Fuel
    - Metallurgical Oils
  - Still Wax
    - Roofing Material
  - Asphalts
    - Liquid Asphalts, Binders, Fluxes
      - Road Oils
      - Roofing Saturants
      - Emulsion Bases
    - Steam Reduced Asphalts
      - Briquetting Asphalts
      - Paving Asphalts
      - Shingle Saturants
      - Paint Bases
      - Flooring Saturants
    - Oxidized Asphalts
      - Roof Coatings
      - Waterproofing Asphalts
      - Rubber Substitutes
      - Insulating Asphalts
  - Coke
    - Carbon Brush Coke
    - Carbon Electrode Coke
    - Fuel Coke
- REFINERY SLUDGES
  - Sulfonic Acid
    - Saponification Agents
    - Demulsifying Agents
  - Heavy Fuel Oils
  - Sulfuric Acid
    - Fertilizers

The gases produced from crude oils are often used within the refinery, although some may be sold locally when allowable by market economics. Motor gasolines are a blend of different product streams, with the final product meeting the specific qualities desired. Numerous additives, for anti-gumming, anti-rust, etc., are also added to motor gasolines and the other fuel products. Very little aviation fuel is produced any more, due to the low level of demand. Jet fuels are utilized by commercial turboprop and jet aircraft. The military also has a portion of its jet fuel produced by the Puget Sound refineries. There is only a small demand for kerosene, so most of this product is blended to make jet fuel. Two of the six types of fuel oil, #1 and #3, are rarely used any more. These are old designations and the product demand has changed sufficiently enough that there is virtually no demand for either of these fuel oils. The remaining products constitute a small fraction of the product yield from the refineries except for asphalt and lubricating oils which are important products of U.S. Oil & Refining and Sound Refining. The products produced by Puget Sound refineries are shown in Table 24.

Determining the exact amount of each product that a specific refinery is producing can be difficult, since this kind of information is often considered to be proprietary. In some instances specific values are available, while in others, only rough estimates can be made from the information that is available. Often instead of the full range of products, the refinery yield is listed under terms like "middle distillates," "residual fuel oils" and "distillate fuel oils" which are groupings of refined products. Also the seasonal variation of product yield makes it necessary to consider an average annual production figure. The availability of specific crude oils may also cause modifications of the "average daily" yield from a refinery. Table 25 shows an estimation of the relative percentages of products produced by the Puget Sound refineries. These are based on information provided by the Federal Energy Administration, the Washington State Department of Ecology, and from the refineries themselves.

2. Mode of Transport

Products produced at Puget Sound refineries are transported by pipeline, railroad car, truck, barge and tanker (Table 26). The Olympic Pipeline originates at the four major refineries in Ferndale and Anacortes, and delivers the refined products to western Washington and Oregon. U.S. Oil & Refining and Sound Refining are not connected to this product pipeline. Since 1972 there has been a gradual increase in the flow of products through the Olympic Pipeline from 171,000 bbls/day to 173,000 bbls/day in 1975, and 184,000 bbls/day during the first half of 1976. This mode of transport accounts for more than 60 percent of the total quantity of products from Mobil, ARCO, Shell and Texaco. These products are predominantly gasolines, with lesser quantities of jet fuel, kerosene and distillate fuel oil, which are all considered "pipeable" products. The pipeline product flow reflects the seasonal shift in refinery products. Generally in summer, gasoline, jet fuel and kerosene make up 60 percent of the volume shipped. In winter this drops to around 50 percent, and the distillate fuel portion (mainly heating oils) rises to 50 percent. Approximately half of these pipeline shipments stay in Washington; the remainder are consumed in Oregon.

Table 24

Petroleum Products Produced by Puget Sound Refineries

Product	Mobil	ARCO	Shell	Texaco	U.S. Oil & Refining	Sound Refining
Motor Gasoline	●	●	●	●	●	
Jet Fuel	●	●	●	●	●	
Domestic Heating Oil	●	●	●	●		
Diesel Fuel Oil (#2)	●	●	●	●	●	
Industrial Heating Oil	●	●	●	●	●	
Bunker C Fuel Oil	●	●	●	●	●	●
Liquefied Petroleum Gas	●	●	●	●		
Petroleum Asphalt					●	●
Lubricating Oils						●
Coke		●				

Table 25

Estimated Relative Percentage of Product Output
by the Puget Sound Refineries from 1974-1976

Product	Mobil	ARCO	Shell	Texaco	U.S. Oil & Refining	Sound Refining
Motor Gasoline	60	44	66	52	51	-
Jet Fuel	29	34	15	38	17	-
Distillate Fuel Oil		12	13		9	-
Residual Fuel Oil	8	8	4	8	3	11
Liquefied Petroleum Gas	3	2	2	2	-	-
Lubricating Oil	-	-	-	-	-	2
Asphalt	-	-	-	-	20	60
Unfinished Distillates	-	-	-	-	-	27

Table 26

Comparison of Land and Marine Transport of the Products Refined by the Puget Sound Refineries

(a) For Mobil, ARCO, Shell and Texaco:

Mode of Transport	1974	1975	1976[§]
Pipeline	52%	52%	56%
Truck, Railroad Car	5%	5%	5%
Marine	43%	43%	39%

[§] First six months

(b) For U.S. Oil & Refining and Sound Refining

Mode of Transport	1974	1975	1976[§]
Truck, Railroad Car	62%	64%	71%
Marine	38%	36%	29%

[§] First six months

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(b) For U.S. Oil & Refining and Sound Refining

Mode of Transport	1974	1975	1976[§]
Truck, Railroad Car	62%	64%	71%
Marine	38%	36%	29%

[§] First six months

A portion of the refined products produced in Washington are shipped around the state by truck or railroad car. This amounts to about ten percent--around 33,000 bbls/day. For the major refineries, this consists of loading tank trucks and rail cars with gasoline and other light products for local consumption. Sound Refining transports some of its asphalt production by truck to local paving companies, as does U.S. Oil & Refining. The remainder of the products produced by Washington and the majority of products consumed in western Washington are transported by tankers and barges.

3. Marine Transport of Petroleum Products

Marine transport accounted for more than 40 percent of the products distributed by Puget Sound refineries in 1974 and 1975. For 1976, an increase in the quantities of products shipped by pipeline has dropped marine traffic to slightly below 40 percent. These marine shipments move products internally to other ports within Puget Sound (defined here to include the Strait of Juan de Fuca beginning at Neah Bay), coastwise to California and other states and to some foreign countries. For 1974, Puget Sound refineries shipped approximately 17.2 million barrels of gasoline, 1.8 million barrels of jet fuel, 0.8 million barrels of kerosene, 8.8 million barrels of distillate fuel oil, and 8.8 million barrels of residual fuel oil, and 0.5 million barrels of other petroleum products.

This movement of petroleum products through Puget Sound accounts for most of the waterborne transport of refined products; however, there is an additional quantity of various products that are imported from foreign sources and other states. Even though approximately 12 million barrels of gasoline were shipped coastwise to other states, Washington ports also received more than 2 million barrels of gasoline by coastwise transport in 1974. This may seem odd, but it is easily accounted for. Petroleum companies, other than those with refineries in the State of Washington, also operate outlets for petroleum products in the state. Hence they import their own particular brand of products, made to their own specifications, to meet market demands. Also, in addition to refined products manufactured by Puget Sound refineries, the military services import a variety of products. The relatively short Buckeye Pipeline serves to transport refined products the seven miles from the Port of Tacoma to McChord Air Force Base.

The total waterborne traffic of petroleum products in the waters of Washington, including products refined in the state and products imported from other sources for 1973 and 1974 is shown in Tables 27, 28, 29, 30, 31, 32, 33, and 34. Each table indicates the receipts and shipments in Puget Sound as a total and by major port; each also is subdivided to distinguish foreign, coastal, internal and local transport, in short tons, of the specific product. This type of detailed information will not be published for 1975 until November of 1976. The "Total" category includes all ports in Puget Sound which receive or ship products. The Ports of Tacoma, Seattle, Anacortes and Bellingham are the principal shippers and recipients of petroleum products. Shipments listed for Bellingham are predominantly from the docks of ARCO and Mobil at Cherry Point and Ferndale, respectively. Shipments listed for Anacortes are primarily from the docks of Shell and Texaco. The sub-category "Coastal" represents all domestic marine traffic

Table 27

Waterborne Transport of Gasoline (in Short Tons) in Puget Sound

Shipping Port or Destination	Receipts		Shipments	
	1973	1974	1973	1974
Total				
Foreign	32,382	47,958	0	0
Coastal	114,410	254,610	1,638,883	1,374,045
Internal	1,406,019	602,599	1,406,019	602,599
Local	75,408	59,178	-	-
Tacoma				
Foreign	4,843	5,454	0	0
California	16,219	0	0	7,597
Oregon	0	0	24,587	0
Internal	170,297	51,899	15,635	16,455
Local	0	1,210	-	-
Seattle				
Foreign	27,539	39,821	0	0
Coastal	89,649	222,829	44,810	18,904
Internal	1,052,724	448,559	322,877	130,496
Local	59,633	22,879	-	-
Anacortes				
California	0	28,723	257,890	595,704
Alaska	0	0	59,848	28,141
Oregon	0	0	45,000	38,174
Hawaii	0	0	61,900	71,310
Internal	601	301	744,872	336,176

Source: (28, 29)

Table 27 (cont.)

Waterborne Transport of Gasoline (in Short Tons) in Puget Sound

Shipping Port or Destination	Receipts		Shipments	
	1973	1974	1973	1974
Bellingham				
Foreign	0	2,683	0	0
California	3,924	0	907,195	367,975
Alaska	0	0	533	2,719
Oregon	0	0	237,082	111,523
East Coast	0	0	0	132,718
Internal	87,318	51,979	318,160	117,929
Local	15,775	35,089	-	-

Table 28

Waterborne Transport of Jet Fuel (in Short Tons) in Puget Sound

Shipping Port or Destination	Receipts 1973	Receipts 1974	Shipments 1973	Shipments 1974
Total				
Foreign	0	0	0	0
Coastal	27,039	42,375	287,634	117,468
Internal	173,173	102,714	173,173	102,714
Local	125,818	204,128	-	-
Tacoma				
Internal	141,844	62,519	15,815	30,822
Local	15,248	73,983	-	-
Seattle				
Coastal	8,481	42,375	63,112	695
Internal	15,514	9,373	0	0
Local	16,720	0	-	-
Anacortes				
California	0	0	23,626	2,112
Alaska	0	0	0	1,910
Oregon	0	0	0	1,437
Hawaii	0	0	0	162
Internal	0	0	9,090	1,385
Bellingham				
California	10,438	0	161,361	81,972
Alaska	8,120	0	6,418	6,399
Oregon	0	0	11,315	22,781
Hawaii	0	0	15,261	0
Internal	15,815	30,822	148,268	67,507
Local	93,850	130,145	-	-

Source: (28, 29)

Table 29

Waterborne Transport of Kerosene (in Short Tons) in Puget Sound

Shipping Port or Destination	Receipts		Shipments	
	1973	1974	1973	1974
Total				
Foreign	248,789	152,589	88,643	71,740
Coastal	3,548	24,546	83,507	31,631
Internal	1,399	7,231	1,399	7,231
Local	702	0	-	-
Tacoma				
Foreign	0	0	8,252	0
Internal	0	0	-	2,125
Seattle				
Foreign	248,789	152,589	0	0
Coastal	3,548	2,641	17,662	449
Internal	1,399	7,231	0	0
Local	702	0	-	-
Anacortes				
California	0	21,905	17,005	11,627
Hawaii	0	0	292	6,607
Bellingham				
Foreign	478	0	80,391	71,740
Oregon	0	0	48,548	12,948
Internal	0	0	1,399	1,274
Local	0	0	-	-

Source: (28, 29)

Table 30

Waterborne Transport of Distillate Fuel Oil (in Short Tons) in Puget Sound

Shipping Port or Destination	Receipts		Shipments	
	1973	1974	1973	1974
Total				
Foreign	75,846	6,999	9,450	14,943
Coastal	785,733	567,284	1,200,385	533,958
Internal	965,441	623,695	965,441	623,695
Local	217,647	92,653	-	-
Tacoma				
Foreign	0	0	9,450	2,028
California	2,970	9,209	0	0
Alaska	0	13,700	0	0
Oregon	0	0	31,054	0
Internal	319,306	161,052	23,885	47,745
Local	1,159	5,452	-	-
Seattle				
Foreign	7,584	6,999	0	0
Coastal	624,108	494,559	54,835	72,329
Internal	457,356	347,884	371,196	176,138
Local	206,438	85,175	-	-
Anacortes				
California	22,575	75,023	25,727	22,749
Alaska	0	0	48,639	10,664
Oregon	0	0	28,713	21,733
Hawaii	0	0	0	6,748
Internal	3,690	1,004	263,755	282,149

Source: (28, 29)

Table 30 (Cont.)

Waterborne Transport of Distillate Fuel Oil (in Short Tons) in Puget Sound

Shipping Port or Destination	Receipts		Shipments	
	1973	1974	1973	1974
Bellingham				
Foreign	68,262	0	0	12,915
California	124,976	0	800,590	350,932
Alaska	0	0	6,611	2,820
Oregon	0	0	194,510	39,599
Hawaii	0	0	9,706	0
Grays Harbor	0	0	0	868
Internal	91,580	63,180	300,183	116,693
Local	10,050	2,026	-	-

Table 31

Waterborne Transport of Residual Fuel Oil (in Short Tons) in Puget Sound

Shipping Port or Destination	Receipts		Shipments	
	1973	1974	1973	1974
Total				
Foreign	17,178	35,469	66,714	137,870
Coastal	709,953	592,216	339,583	793,576
Internal	399,704	362,845	399,704	362,845
Local	233,116	128,954	-	-
Tacoma				
Foreign	0	0	0	8,984
California	22,461	0	0	0
Internal	159,134	100,593	7,717	6,542
Local	11,751	7,075	-	-
Seattle				
Foreign	10,696	35,469	4,050	6,750
Coastal	393,388	336,697	92,240	40,929
Internal	159,794	148,986	141,319	128,787
Local	220,326	118,402	-	-
Anacortes				
California	0	33,302	24,645	52,051
Alaska	0	0	8,132	0
Oregon	0	0	0	23,723
Hawaii	0	0	2,455	1,053
Grays Harbor	0	0	0	6,936
Internal	1,172	32,833	182,885	172,938
Local	1,039	0	-	-

Source: (28, 29)

Table 31 (Cont.)

Waterborne Transport of Residual Fuel Oil
(in Short Tons) in Puget Sound

Shipping Port or Destination	Receipts		Shipments	
	1973	1974	1973	1974
Bellingham				
Foreign	6,482	0	62,664	122,136
California	143,465	131,262	212,111	668,884
Oregon	18,529	0	0	0
Internal	19,130	20,077	67,782	54,578
Local	0	3,477	-	-

Table 32

Waterborne Transport of Lube Oils and Greases (in Short Tons) in Puget Sound

Shipping Port or Destination	Receipts		Shipments	
	1973	1974	1973	1974
Total				
Foreign	27	129	1,174	3,203
Coastal	142,478	102,418	27,416	22,669
Tacoma				
Foreign	0	0	337	198
Coastal	15,012	0	0	0
Seattle				
Foreign	27	129	837	2,998
Coastal	89,551	72,320	7,640	21,052
Anacortes				
Coastal	37,915	16,940	0	0
Bellingham				
Coastal	0	0	19,776	1,617

Source: (28, 29)

Table 33

Waterborne Transport of Naphtha, Petroleum Solvents (in Short Tons) in Puget Sound

Shipping Port or Destination	Receipts		Shipments	
	1973	1974	1973	1974
Total				
Coastal	22,277	39,380	1,540	28,578
Internal	9,431	6,427	9,431	6,427
Tacoma				
Internal	9,431	5,702	0	0
Seattle				
Coastal	22,277	19,210	1,540	330
Internal	0	0	0	725
Anacortes				
Coastal	0	20,170	0	28,248
Bellingham				
Internal	0	725	9,431	5,702

Source: (28, 29)

Table 34

Waterborne Transport of Asphalt, Tar and Pitches (in Short Tons) in Puget Sound

Shipping Port or Destination	Receipts		Shipments	
	1973	1974	1973	1974
Total				
Coastal	219,152	162,799	11,454	8,357
Internal	326	0	326	0
Local	4,775	0	-	-
Tacoma				
Coastal	3,405	0	0	0
Seattle				
Coastal	215,747	162,799	11,454	8,357
Internal	0	0	326	0
Local	4,775	0	-	-
Anacortes				
Coastal	0	0	0	0
Bellingham				
Internal	326	0	0	0

Source: (29, 29)

that enters or leaves Puget Sound. As often as possible, specific states are named as shipping ports or destinations of the refined products. Movement of crude within Puget Sound is indicated under "Internal". "Local" transport is within the confines of an individual harbor or port and has been arbitrarily designated as a receipt (a "-" appears under shipments).

The relationship between the eight categories employed by the Army Corps of Engineers (which publishes these data) and the actual products produced by the refineries is:

- Gasoline: includes all grades of motor gasoline and a small percentage of aviation gasoline used by small piston planes.
- Jet Fuel: same as refinery products.
- Kerosene: same as refinery products.
- Distillate Fuel Oil: includes fuel oils #1, #2, #3, and #4, but is predominantly #2 diesel fuel oils with some #4 heating oil. Also may include some stove oil and kerosenes.
- Residual Fuel Oil: includes fuel oils #5 and #6, but mostly #6 Bunker "C" fuel oils.
- Lubricating Oils and Greases: same as refinery products.
- Naphtha, Petroleum Solvents: includes some straight run naphtha, kerosenes, stove oil made into commercial solvents.
- Asphalt, Tar and Pitches: same as refinery products.

Most of the products refined by the Puget Sound refineries that are transported by marine vessels are shipped coastwise to other states, mainly California. Kerosene, which comprises about four percent of the marine-transported petroleum products is the one notable exception. Most of the kerosene is shipped to foreign countries. Consideration of the total waterborne transport of refined products yields similar results. For each of the products, most of the marine traffic moves to or from other states, except for kerosene which is predominantly received from and delivered to, foreign countries (Tables 35 and 36).

4. Chemical Composition and Characteristics of Refined Products

The compounds present in refined products are similar to those found in crude oils with the addition of the olefin class of hydrocarbons. Olefins are formed in refinery processes involving the cracking of the feedstock. Olefins are utilized as feedstock in alkylation and polymerization processes to yield high octane blending components for motor gasoline and some jet fuel. These compounds are partially unsaturated due to the presence of at least one double bond, and are more reactive than paraffin and naphthene hydrocarbons, but not as reactive for substitution as aromatics. Table 37 shows some of the predominant olefin hydrocarbons. Refined products also contain a number of sulfur, nitrogen and oxygen-containing compounds, along with various product additives designed to make the product perform more efficiently.

Table 35

Percentage of Waterborne Transport of Petroleum Products in 1973 on Puget Sound According to Source or Destination

Petroleum Products	Foreign	Coastal	Internal	Local
Motor Gasoline	1	54	43	2
Jet Fuel	0	51	28	21
Kerosene	79	20	<1	<1
Distillate Fuel Oil	2	61	30	7
Residual Fuel Oil	5	59	23	13
Lubricating Oil and Greases	1	99	0	0
Naphtha, Petroleum Solvents	0	72	<8	0
Asphalt, Tar and Pitches	0	98	<1	2

Table 36

Percentage of Waterborne Transport of Petroleum Products in 1974 on Puget Sound According to Source or Destination

Petroleum Products	Foreign	Coastal	Internal	Local
Motor Gasoline	2	69	26	3
Jet Fuel	0	34	22	44
Kerosene	77	20	3	0
Distillate Fuel Oil	1	60	34	5
Residual Fuel Oil	8	68	18	6
Lubricating Oil and Greases	3	97	0	0
Naphtha, Petroleum Solvents	0	92	8	0
Asphalt, Tar and Pitches	0	100	0	0

Table 37

Some Typical Olefinic Hydrocarbon Compounds

Name		Formula	Melting Point		B. P. at 760 mm.		Sp. Gr. at °C.
			(°F.)	(°C.)	(°F.)	(°C.)	
Ethylene	C_2H_4	$CH_2=CH_2$	−272.9	−169.4	−154.8	−103.8	0.566 (−102°)
Propene	C_3H_6	$CH_2=CH—CH_3$	−301.4	−185.2	−53.9	−47.7	0.610 (−47°)
Butenes							
1-Butene (ethylethylene)	C_4H_8	$CH_2=CH—CH_2—CH_3$	−202	−130	19.9	−6.7	0.617 (0°)
2-Butene (*cis* and *trans* mixture)	C_4H_8	$CH_3—CH=CH—CH_3$	−198.6	−127	32–37.4	0−3	0.628 (1.7°)
2-Methylpropene (isobutene)	C_4H_8	$CH_2=C(CH_3)—CH_3$	−232.6	−140.7	20.1	−6.6	0.627 (−6.6°)
Pentenes							
1-Pentene	C_5H_{10}	$CH_2=CH—(CH_2)_2—CH_3$			86.2	30.1	0.642 (20°)
2-Pentene (*cis* and *trans* mixture)	C_5H_{10}	$CH_3—CH=CH—C_2H_5$	−218.2	−139	97.5	36.4	0.651 (20°)
2-Methyl-1-butene	C_5H_{10}	$CH_2=C(CH_3)—CH_2—CH_3$			87.8	31	0.650 (20°)
3-Methyl-1-butene	C_5H_{10}	$CH_2=CH—CH(CH_3)—CH_3$	−211	−135	68.2	20.1	0.632 (15°)
2-Methyl-2-butene	C_5H_{10}	$CH_3—C(CH_3)=CH—CH_3$	−191.2	−124	101.1	38.4	0.662 (20°)
1-Hexene	C_6H_{12}	$CH_2=CH—(CH_2)_3—CH_3$			146.1	63.4	0.679 (20°)
1-Heptene	C_7H_{14}	$CH_2=CH—(CH_2)_4—CH_3$	−182.2	−119	199.4	93	0.698 (20°)
1-Octene	C_8H_{16}	$CH_2=CH—(CH_2)_5—CH_3$			253.4	123	0.717 (20°)
1-Nonene	C_9H_{18}	$CH_2=CH—(CH_2)_6—CH_3$			294.8	146	0.730 (20°)
1-Decene	$C_{10}H_{20}$	$CH_2=CH—(CH_2)_7—CH_3$			341.6	172	0.763 (0°)
1-Undecene	$C_{11}H_{22}$	$CH_2=CH—(CH_2)_8—CH_3$			370.4	188	0.763 (20°)
1-Dodecene	$C_{12}H_{24}$	$CH_2=CH—(CH_2)_9—CH_3$	−24.7	−31.5	415.4	213	0.762 (15°)
1-Tridecene	$C_{13}H_{26}$	$CH_2=CH—(CH_2)_{10}—CH_3$			450.9	232.7	0.798 (20°)
1-Tetradecene	$C_{14}H_{28}$	$CH_2=CH—(CH_2)_{11}—CH_3$	10.4	−12	474.8	246	0.775 (20°)
1-Hexadecene (cetene)	$C_{16}H_{32}$	$CH_2=CH—(CH_2)_{13}—CH_3$	39.2	4	525.2	274	0.784 (20°)
1-Octadecene	$C_{18}H_{36}$	$CH_2=CH—(CH_2)_{15}—CH_3$	64.4	18	593.6	312	0.791 (20°)

Table 6. Diolefin Hydrocarbons.

Name		Formula	Melting Point		B. P. at 760 mm.		Sp. Gr. at 20° C.
			(°F.)	(°C.)	(°F.)	(°C.)	
Propadiene (allene)	C_3H_4	$CH_2=C=CH_2$	−213	−136.1	−29.7	−34.3	
1,3-Butadiene (erythrene)	C_4H_6	$CH_2=CH—CH=CH_2$			23	−5	0.610
1,3-Pentadiene (piperylene)	C_5H_8	$CH_2=CH—CH=CH—CH_3$			109.4	43	0.680
2-Methyl-1,3-butadiene (isoprene)	C_5H_8	$CH_2=C(CH_3)—CH=CH_2$	−232.2	−146.8	93.2	34	0.681
2,3-Dimethyl-1,3-butadiene (diisopropenyl)	C_6H_{10}	$CH_2=C(CH_3)—C(CH_3)=CH_2$	−104.8	−76	156.4	69.1	0.726
1.5-Hexadiene (diallyl)	C_6H_{10}	$CH_2=CH—CH_2—CH_2—CH=CH_2$	−221.8	−141	140	60	0.688
2-4-Dimethyl-1,3-pentadiene	C_7H_{12}	$CH_2=C(CH_3)—CH=C(CH_3)—CH_3$			199.4	93	0.737
2,5-Dimethyl-1,5-hexadiene	C_8H_{14}	$CH_2=C(CH_3)—CH_2—CH_2—C(CH_3)=CH_2$			235.4	113	0.740
2,6-Dimethyl-1,5-heptadiene	C_9H_{16}	$CH_2=C(CH_3)—CH_2—CH_2—CH=C(CH_3)—CH_3$			285.8	141	0.765

Source: (18)

From CHEMICAL REFINING OF PETROLEUM
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a. Liquefied Petroleum Gases (LPG). Liquefied petroleum gases are composed of those readily liquefiable hydrocarbon compounds which are produced in the course of refining crude oil. There are many important uses of these liquefied gases including: commercial, domestic and industrial fuels; raw materials for synthetic gasoline production; and petrochemical plant feedstock. There are four basic types of liquefied petroleum gases which are covered by the American Society for Testing and Materials (ASTM) specifications: commercial propane; butane; propane-butane mixtures; and special-duty propane. Commercial propane is preferred for domestic, commercial and industrial use in areas where low temperatures are common. This type of LPG has a very high volatile content. Commercial butane has a lower volatility and is used by industrial and commercial users in areas where low temperatures are not a serious problem. The propane-butane mixtures provide an intermediate volatility. Special-duty propane fuel is specifically tailored to meet the qualifications of the proposed function. Table 38 indicates the ASTM specifications for liquefied petroleum gases. The hydrocarbon content of these liquefied gases are C_3 and C_4 hydrocarbons and are virtually 100 percent paraffinic. The volatility of these liquefied gases is very high when compared to the other refined products.

b. Motor Gasoline. Gasoline is composed of a mixture of paraffinic, naphthenic, olefinic, and aromatic hydrocarbons which are generally distilled from crude oils at temperatures ranging up to 300-350°F. The exact composition will vary within the specification limits for the individual product, and will depend on the blending components utilized to yield the product. Motor gasoline may be a blend of straight run gasoline, reformed gasoline, polymerized gasoline, alkylation gasoline, hydrogenated gasoline, and cracked gasoline fractions. Blending is important because a fraction from a single operation usually cannot meet commercial specifications. Many of these fractions are produced by processes designed to upgrade the octane rating of the final product. Examples of the composition of two typical blending components are shown in Table 39.

The hydrocrackate fraction is used for blending both jet fuel and motor gasoline, and the table indicates the relative yields and properties of both products when refinery operations are emphasizing one fuel over the other. This also provides a good indication of the fluctuation of the hydrocarbon composition of products resulting from variations in the refinery process operations. Straight run gasoline in general is composed of 50 percent paraffins, 40 percent naphthenes, and 10 percent aromatics. The final composition of motor gasolines varies within the specifications for the particular grade of gasoline and varies with the amounts and types of additives utilized. Typically though, motor gasoline contains C_5-C_{10} compounds which are approximately 35-50 percent paraffins, 25-45 percent naphthenes, and 10-35

Table 38

ASTM Specifications for Liquefied Petroleum Gas

	Product Designation				
	Commercial Propane	Commercial Butane	Commercial PB Mixtures	Special-Duty Propane[a]	ASTM Test Methods (see Section 2)
Vapor pressure at 100°F (37.8°C), max, psig	208	70	[b]	208	D 1267 or
kPa	1430	485		1430	D 2598
Volatile residue:					
evaporated temperature, 95 %, max, °F	−37	36	36	−37	
°C	−38.3	2.2	2.2	−38.3	D 1837
or					
butane and heavier, max, %	2.5	. . .	. . .	2.5	D 2163
pentane and heavier, max, %	. . .	2.0	2.0	. . .	D 2163
Propylene content, max, %	. . .	. . .	. . .	5.0	D 2163
Residual matter:					
residue on evaporation 100 ml, max, ml	0.05	0.05	0.05	0.05	D 2158
oil stain observation	pass[c]	pass[c]	pass[c]	pass[c]	D 2158
Relative density (specific gravity) at 60/60°F (15.6/15.6°C)	[d]	[d]	[d]	. . .	D 1657 or D 2598
Corrosion, copper, strip, max	No. 1	No. 1	No. 1	No. 1	D 1838
Sulfur, grains/100 ft³ max at 60°F and 14.92	15	15	15	10	
psia mg/m³ max at 15.6°C and 101 kPa	343	343	343	229	D 2784
Hydrogen sulfide content	. . .	. . .	. . .	pass[e]	D 2420
Moisture content	pass[f]	. . .	. . .	pass[f]	
Free water content	. . .	none[g]	none[g]	. . .	

[a] Equivalent to Propane HD-S of GPA Publication 2140.

[b] The permissible vapor pressures of products classified as PB mixtures must not exceed 200 psig (1380 kPa) and additionally must not exceed that calculated from the following relationship between the observed vapor pressure and the observed specific gravity:

Vapor pressure, max = 1167 − 1880 (sp gr 60/60°F) or 1167 − 1880 (density at 15°C)

A specific mixture shall be designated by the vapor pressure at 100°F in pounds per square inch gage. To comply with the designation, the vapor pressure of the mixture shall be within +0 to −10 psi of the vapor pressure specified.

[c] An acceptable product shall not yield a persistent oil ring when 0.3 ml of solvent residue mixture is added to a filter paper, in 0.1-ml increments and examined in daylight after 2 min as described in Method D 2158.

[d] Although not a specific requirement, the specific gravity must be determined for other purposes and should be reported. Additionally, the specific gravity of PB mixture is needed to establish the permissible maximum vapor pressure (see Footnote *b*).

[e] An acceptable product shall not show a distinct coloration.

[f] Use one of the alternate methods for moisture content as described in the Propane Dryness Test, Cobalt Bromide Method, or Dew Point Method of GPA Publication 2140.

[g] The presence or absence of water shall be determined by visual inspection of the samples on which the gravity is determined.

Source: (11)

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Table 39

General Characteristics of Reformate and Hydrocrackate, Two Gasoline Blending Components, Produced at the ARCO Cherry Point Refinery

Reformate

Gravity, °API	24.3
Distillation, D-1160, °F.	
Ibp	556
10	680
50	773
90	870
Ep	925
Sulfur, wt %	0.95
Nitrogen, ppm	1,780
Hydrocarbon type, wt %	
Paraffins	17.7
Olefins	5.4
Naphthenes	28.0
Aromatics	35.5
Heterocyclics	13.4

Hydrocrackate

Typical results	Operation 1	Operation 2
Dry gas, scf/bbl feed		
C_1-C_3	62	99
Liquid products, vol % feed		
iC_4	5.6	8.8
nC_4	2.3	4.3
C_5-C_6	18.9	26.2
C_7-315° F.	39.0	55.2
Jet fuel	56.0	30.0
Total C_4+	121.8	124.5
Hydrogen consumption chemical, scf/bbl feed	1,820	2,080
Product properties		
C_7-315° F.		
Gravity, °API	57.5	56.1
Hydrocarbon type, vol %		
Paraffins	39.0	36.0
Naphthenes	56.5	57.9
Aromatics	4.5	6.1
Octane, F-1 + 3 ml TEL	80.5	81.2
JET FUEL		
Gravity, °API	45.3	46.7
Aromatics, vol %	11.5	7.5
Smoke point, mm	25	28
Sulfur, ppm	<5	<5

*Jet-fuel yield changed by factor of almost two. Typical results, pilot-plant simulation.

Source: (1)

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Aalund, Leo, 1972. "Cherry Point Refinery",
Oil and Gas Journal, Vol. 70, No. 4
65-72.

percent aromatics and 5-15 percent olefins. A very large percent of these hydrocarbons are highly volatile and somewhat soluble in water.

c. Jet Fuel. Jet fuel or aviation turbine fuel is composed of straight run naphtha and kerosene, along with some cracked stock. There are four basic grades of jet fuel: Jet A, Jet A-1, JP-4, and JP-5. The latter two grades are primarily for military use. Additives may be present in these fuels in accordance with composition specifications. These include electrical conductivity additives, antioxidants, metal deactivators, corrosion inhibitors, fuel system icing inhibitors and other special purpose additives (Table 40).

Generally jet fuels have boiling points ranging from approximately 400-570°F and contain hydrocarbons mainly in the C_{10}-C_{12} molecular weight range. Jet fuels contain all four classes of hydrocarbons, although very few olefins. Typically jet fuels are composed of about 35 percent paraffins, 50 percent naphthenes, and 15 percent aromatics. In general, paraffins are more desirable than other hydrocarbon compounds because of the characteristic of cleaner combustion. Naphthenes are the next most desirable hydrocarbons for jet fuels in terms of combustion characteristics. Olefins have good combustion characteristics too, but their gum stability is poor, limiting their usefulness in aircraft turbine fuels. Aromatic hydrocarbons have the least desirable combustion characteristics, tending to be smoky and leave a carbon deposit. According to the ASTM specifications (D 1655-75), it is desirable to have no more than 20 percent aromatics in Jet A and Jet A-1 fuel (Table 41). Military specifications for JP-4 and JP-5 jet fuels allow up to 25 percent aromatics (Table 42). Olefin hydrocarbon content usually is only one percent, although it can be as high as three percent of a jet fuel.

d. Kerosene. Kerosene is employed primarily for heating and lighting purposes. Its average boiling point is above that of gasoline and ranges from 300-600°F. The burning quality of kerosene is adversely affected by aromatic hydrocarbons, so it is desirable to keep the percentage of aromatics low. The typical hydrocarbon composition of these C_{10}-C_{12} compounds is 40 percent paraffins, 45 percent naphthenes and 15 percent aromatics. In general though, the demand for kerosene and similar products has not kept pace with the amount of kerosene stock produced. Therefore, much of the stock is converted into petroleum solvents or processed through cracking operations into lower-boiling hydrocarbons suitable for motor gasoline or jet fuel blending stocks.

e. Fuel Oils. Fuel oils include both distillates and residual fractions and serve a wide variety of purposes. The specifications vary with the type of fuel oil and the expected performance desired. In general, the volatility decreases and the viscosity increases when comparing fuel oils #1 through #6. Additives found in fuel oils

Table 40

Examples of Specific Antioxidant Additives Allowed by Military Specifications in JP-4 and JP-5 Jet Fuel

Antioxidants. The following active inhibitors may be blended separately or in combination into the fuel in total concentration not in excess of 8.4 pounds of inhibitor (not including weight of solvent) per 1,000 barrels of fuel (9.1 g/100 gal (US), 24 mg/liter or 109 mg/gal (UK)) in order to prevent the formation of gum:

a. N,N' diisopropyl-*p*-phenylenediamine

b. N,N'-di-*sec*-butyl-*p*-phenylenediamine

c. 2,6-di-*tert*-butyl-4-methylphenol

d. 6-*tert*-butyl-2,4-dimethylphenol

e. 2,6-di-*tert*-butylphenol

f. 75 percent min-2,6-di-*tert*-butylphenol
25 percent max *tert*-butylphenols and tri-*tert*-butylphenols

g. 72 percent min 6-*tert*-butyl-2,4-dimethyphenol
28 percent max *tert*-butyl-methylphenols and *tert*-butyl-dimethylphenols

h. 55 percent min 6-*tert*-butyl-2,4-dimethylphenol
45 percent max mixture of *tert*-butylphenols and di-*tert*-butylphenols

i. 65 percent N,N'-di-*sec*-butyl-*p*-phenylenediamine
35 percent N,N'-di-*sec*-butyl-*o*-phenylenediamine

j. 60 to 80 percent 2,6-dialkylphenols
20 to 40 percent mixture of 2,3,6-trialkylphenols and 2,4,6-trialkylphenols

k. 35 percent min 2,6-di-*tert*-butyl-4-methylphenol
65 percent max mixture of methyl-, ethyl-, and dimethyl-*tert*-butylphenols

l. 60 percent min 2,4-di-*tert*-butylphenol
40 percent max mixture of *tert*-butylphenols

m. 30 percent min mixture of 2,3,6-trimethylphenol and 2,4,6,-trimethylphenol
70 percent max mixture of dimethylphenols

n. 65 percent mixture of 2,4,5-triisopropylphenol and 2,4,6-triisopropylphenol
35 percent max mixture of other isopropylphenols and biphenols

Source: (30)

Table 41

ASTM Specifications for Jet A and Jet A-1 Fuels

Property	Jet A or Jet A-1	Jet B	ASTM Test Method[b]
Acidity, total max, mg KOH/g	0.1	. . .	D 974 or D 3242
Aromatics, vol, max, %	20	20	D 1319
Sulfur, Mercaptan,[c] wt, max, %	0.003	0.003	D 1323 or D 1219
Sulfur, total wt, max, %	0.3	0.3	D 1266
Distillation temperature, °F (°C):			D 86
10% recovered, max, temp	400 (204.4)	. . .	
20% recovered, max, temp	. . .	290 (143.3)	
50% recovered, max, temp	report	370 (187.8)	
90% recovered, max, temp	report	470 (243.3)	
Final boiling point, max, °F (°C)	572 (300)	. . .	
Distillation residue, max, %	1.5	1.5	
Distillation loss, max, %	1.5	1.5	
Flash point, min, °F (°C)	100 (37.8)		D 56 or D 3243
Gravity, max, °API (min, sp gr) at 60°F	51 (0.7753)	57 (0.7507)	D 1298
Gravity, min, °API (max, sp gr) at 60°F	37 (0.8398)	45 (0.8017)	D 1298
Vapor pressure, max, lb	. . .	3	D 323
Freezing point, max, °C	−40[d] Jet A −50[d] Jet A-1	−50[d]	D 2386
Viscosity −30°F (−34.4°C) max, cSt	15	. . .	D 445
Net heat of combustion, min, Btu/lb	18.400[e]	18.400[e]	D 1405 or D 2382
Combustion properties: one of the following requirements shall be met:			
(1) Luminometer number, min or	45	45	D 1740
(2) Smoke point, min or	25	25	D 1322
(3) Smoke point, min	20	20	D 1322
Naphthalenes, vol, max, % or	3		D 1840
Corrosion, copper strip 2 h at 212°F (100°C) min	No. 1	No. 1	D 130
Thermal stability: one of the following requirements shall be met:			
(1) Filter pressure drop, max, in. Hg	3	3	D 1660[f]
Preheater deposit less than	Code 3	Code 3	
(2) Filter pressure drop, max, mm Hg	25	25	D 3241[g]
Tube deposit less than	Code 3	Code 3	
Existent gum, mg/100 ml, max	7	7	D 381
Water reaction:			
Separation rating, max	2	2	D 1094
Interface rating, max	1b	1b	D 1094
Additives	See 4.2		
Electrical conductivity, pS/m	[h]	[h]	D 2624 or D 3114

[a] The requirements herein are absolute and are not subject to correction for tolerance of the test methods. If multiple determinations are made, average results shall be used.

[b] The test methods indicated in this table are referred to in Section 9.

[c] The mercaptan sulfur determination may be waived if the fuel is considered sweet by the doctor test described in 4.2 of Specification D484, for Hydrocarbon Drycleaning Solvents.[8]

[d] Other freezing points may be agreed upon between supplier and purchaser.

[e] Use for Jets A and A-1 the value calculated from Table 8 or Eqs 5, and 9 in Method D 1405. Use for Jet B the value calculated from Table 6 or Eqs 5, and 7 in Method D 1405. Method D 2382 may be used as an alternative. In case of dispute, Method D 2382 must be used.

[f] Thermal stability test shall be conducted for 5 h at 300°F (148.9°C) preheater temperature 400°F (204.4°C) filter temperature, and at a flow rate of 6 lb/h.

[g] Thermal stability test (JFTOT) shall be conducted for 2.5 h at a control temperature of 260°C but if the requirements of Table 1 are not met, the test may be conducted for 2.5 h at a control temperature of 245°C. Results at both test temperatures shall be reported in this case. Tube deposits shall always be reported by the Visual Method; a rating by the Tube Deposit Rating (TDR) optical density method is desirable but not mandatory.

[h] A limit of 50 to 300 conductivity units (pS/m) applies only when an electrical conductivity additive is used and under the condition at point of use:

$$1\ \mathrm{pS/m} = 1 \times 10^{-12}\ \Omega^{-1}\,\mathrm{m}^{-1}$$

Source: (11)

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Table 42

Military Specifications for JP-4 and JP-5 Jet Fuels

Requirements	Fuel		Test Method
	Grade JP-4	Grade JP-5	ASTM Standards
Color, Saybolt	1/	1/	D 156
Total acid number, mg KOH/g, max	0.015	0.015	D 3242
Aromatics, vol percent, max	25.0	25.0	D 1319
Olefins, vol percent max	5.0	5.0	D 1319
Mercaptan sulfur, weight percent, max 2/	0.001	0.001	D 1323
Sulfur, total weight percent, max	0.40	0.40	D 1266, D 1552, D 2622
Distillation temperature, deg C, (D 2887 limits in parentheses)			D 86 3/ or D 2887
Initial boiling point	1/	1/	
10 percent recovered, max temp	1/	205 (185)	
20 percent recovered, max temp	145 (130)	1/	
50 percent recovered, max temp	190 (185)	1/	
90 percent recovered, max temp	245 (250)	1/	
End point, max temp	270 (320)	290 (320)	
Residue, vol percent, max (for D 86)	1.5	1.5	
Loss, vol percent, max (for D 86)	1.5	1.5	
Explosiveness percent, max	--	50	4/
Flash point, deg C (deg F), min	--	60 (140)	D 93
Density, kg/m^3, min (^{o}API, max) at 15^{o}C	751 (57.0)	788 (48.0)	D 1298
Density, kg/m^3, max (^{o}API, min) at 15^{o}C	802 (45.0)	845 (36.0)	D 1298
Vapor pressure, 37.8^{o}C (100^{o}F), kPa (psi), min	14 (2.0)	--	D 323 or D 2551
Vapor pressure, 37.8^{o}C (100^{o}F), kPa (psi), max	21 (3.0)	--	D 323 or D 2551
Freezing point, deg C (deg F), max	-58 (-72)	-46 (-51)	D 2386
Viscosity, at -20^{o}C, max, mm^2/s(centistokes)	--	8.5 (8.5)	D 445
Heating value, Aniline-gravity product, min,	5,250	4,500	D 1405
or Net heat of combustion, MJ/kg (Btu/lb) min	42.8 (18,400)	42.6 (18,300)	D 240, D 2382 or D 3338 5/
Hydrogen content, wt percent, min	13.6	13.5	D 1018 or 3343 6/
or Smoke point, mm, min	20.0	19.0	D 1322

Table 42 (cont.)

Requirements	Fuel		Test Method
	Grade JP-4	Grade JP-5	ASTM Standards
Copper strip corrosion, 2 hr at 100°C (212°F) max	1b	1b	D 130
Thermal stability:			
Change in pressure drop, mm of Hg., max	25	25	D 3241 7/
Preheater deposit code, less than	3	3	
Existent gum, mg/100 ml, max	7.0	7.0	D 381
Particulate matter, mg/liter, max	1.0	1.0	D 2276 8/
Filtration time, minutes, max	15	--	8/
Water reaction			
Interface rating, max	1b	--	D 1094
Separation rating, max	1	--	
Water separation index, modified, min	70	85	D 2550
Fuel system icing inhibitor, vol percent min	0.10	0.10	9/
Fuel system icing inhibitor, vol percent max	0.15	0.15	9/

1/ To be reported - not limited.

2/ The mercaptan sulfur determination may be waived at the option of the inspector if the fuel is "doctor sweet" when tested in accordance with the doctor test of ASTM D 484.

3/ A condenser temperature of 32° to 40°F (0° to 4°C) shall be used for the distillation of grade JP-5. For JP-4, use group 3 test conditions. Distillation shall not be corrected to 760 mm pressure.

4/ Test shall be performed in accordance with method 1151 Federal Standard 791.

5/ ASTM D 3338, for calculating the heat of combustion, is only allowed for use with JP-4 fuel. When the fuel distillation test is also performed using ASTM D 2887, the average distillation temperature, for use in ASTM D 3338, shall be calculated as follows:

$$V = \frac{10\% + 50\% + 95\%}{3}$$

Table 42 (cont.)

6/ ASTM D 3343, for calculating the hydrogen content of the fuel, is only allowed for use with JP-4 fuel. When the fuel distillation test is also performed using ASTM D 2887, the average distillation temperature for use in D 3343 shall be calculated as follows:

$$V = \frac{10\% + 50\% + 95\%}{3}$$

7/ See 4.7.1.1 for ASTM D 3241 test conditions and test limits.

8/ A minimum sample size of one gallon shall be filtered. Filtration time will be determined in accordance with the procedure of Appendix A. The procedure in Appendix A may also be used for the determination of particulate matter as an alternate to ASTM D 2276.

9/ Test shall be performed with method 5327 of Federal Standard 791.

Source: (30)

vary, but may include metal deactivators, stabilizers, dispersants, cetane improvers, flow improvers, and conductivity improvers.

The distillate fuel oils, #1 (rare), #2, #3 (rare), and #4, are a middle fraction of crude petroleum with some mixture of catalytic or thermally cracked components. Chemically these fuel oils are composed almost entirely of hydrocarbons within the range of C_{12}-C_{25} with the greatest abundance at C_{15}-C_{16}. Generally these fuels contain about 30 percent paraffins, 45 percent naphthenes and 25 percent aromatics. When blended, there are fewer naphthenes and paraffins and more olefins and aromatics. In some diesel fuel oils (#2), the aromatic content may be as high as 40 percent. In general, however, the aromatic content does not vary greatly from one distillate fuel oil to another.

For three major grades of diesel fuel oil, #1-D, #2-D, and #4-D, the ASTM specifications are less concerned with hydrocarbon content; instead, the volatility is a more important factor in the performance of the fuel. The fuel volatility requirements vary with engine design, size, nature of speed and load variations and on starting conditions. Diesel fuel oil #1-D is made from kerosene and intermediate distillates to provide the desired high amount of volatiles. This fuel is used widely by buses and trucks. Grade #2-D is made from distillate gas oils and has a corresponding lower quantity of volatiles. The lower distillates are blended with some residual fractions to yield grade #4-D diesel fuel, which is highly viscous and much lower in volatiles.

Residual fuel oils #5 and #6 are high viscosity oils and often require preheating to permit pumping. Most of the contaminants that are in crude oils which are not removed during the refining process can be found in these heavy oils. Nickel, vanadium, sulfur and heavy metals are much more abundant than in other products. Specific percentages will depend on the nature of the crude oils and the processes involved. Additional refining may be necessary to accommodate areas with air quality problems, particularly regarding sulfur content. Chemically the majority of hydrocarbon compounds are above C_{25} for #5 fuel oil and above C_{30} for #6 fuel oil (Bunker C). Typically, residual fuel oils contain approximately 15 percent paraffins, 45 percent naphthenes, 25 percent aromatics, and 15 percent polar non-hydrocarbon compounds. These non-hydrocarbon nitrogen, oxygen and sulfur-containing compounds are very easily dissolved in seawater because of their polarity. The rate of solution will depend on the gravity, viscosity, pour point, surface tension and other factors. In general, the specifications for fuel oils of all types are not concerned with hydrocarbon content beyond the percentage of volatiles. Viscosity, pour point, and sulfur content are more important factors affecting the functioning of the fuel and these are more closely examined when fuel oils are analyzed.

f. Lubricating Oils and Greases. Lubricating oils serve a variety of different purposes, including lubricating machinery. Lubricating oil stock is usually considered to include distillates obtainable from crude oil after the gas oil fractions have been expelled, as well as some of the residual fractions from light crude oils. These residuals are particularly common in the manufacture of motor and airplane engine oils. When a heavy asphaltic crude is refined, distillates provide the stock for lubricating oils. Lubricating oils which are rendered semi-solid or solid by addition of soaps and similar materials are classified as greases. Thus the hydrocarbon composition of lubricating oils and greases is highly variable, depending on which refined fractions are involved, but generally lies within the range C_{10}-C_{25}. No specifications regarding the quantities of specific classes of hydrocarbons are made for these products. Some estimations of hydrocarbon content indicate 20-40 percent paraffins, 30-55 percent naphthenes, and 15-45 percent aromatics.

g. Naphtha and Petroleum Solvents. Certain petroleum fractions boiling in the range of 200-600°F, which includes straight run naphtha and kerosene, are utilized as commercial solvents. These petroleum fractions are used in the manufacture of cleaners' naphtha, Stoddard's solvent, rubber solvent, lacquer, paint thinner, and other refined products. Generally, the range of molecular weights is C_{10}-C_{12}, the same as kerosene. In contrast to a desirable kerosene, such solvents often contain aromatic hydrocarbons to enhance their solubility characteristics. Frequently, these petroleum solvents are made from aromatic material extracted from kerosene stock during the course of refining. The hydrocarbon content of these different types of solvents is variable but generally ranges from 20-35 percent paraffins, 30-45 percent naphthenes, and 20-50 percent aromatics. These solvents also have a relatively high portion of volatile compounds.

h. Asphalt and Coke. The term "asphalt" in the petroleum industry applies to the semi-solid or solid residuum left after the volatile fractions have been removed. If distillation is carried to completion, with sufficient time, the residue becomes coke. Petroleum asphalt is used in the manufacture of paving asphalt, for impregnating roofing paper, and for other similar purposes. Coke is often used for industrial processing in making steel. The hydrocarbon content of asphalt depends on the type of crude that is processed initially. The majority of compounds have a molecular size of C_{40} or higher. Asphalt also contains very few volatiles, due to the repeated distillation of lighter products. Coke is essentially solid carbon, with some hydrogen and other impurities. It also has virtually no volatile compounds.

i. Relative Toxicities of Refined Products. Although non-hydrocarbon substances occur in petroleum products, the predominant constituents are hydrocarbons and these compounds are responsible for virtually all the biological effects attributed to refined products. As with crude oils, the relative toxicity of the classes of hydrocarbons increases from paraffins to naphthenes to olefins to aromatics. Table 43 summarizes the relative percentages of hydrocarbon compounds found in refined products. The water solubility and the presence of volatiles also influence the toxicity of petroleum products. In general the more soluble and volatile a particular hydrocarbon is, within a given chemical class, the greater the toxicity of the compound. A number of researchers have provided evidence that the lower boiling, more soluble aromatic hydrocarbons are consistently the primary cause of the mortality of marine organisms exposed to refined products. Other aromatic compounds, and naphthenic and paraffinic hydrocarbons also contribute to the toxic effects of petroleum products.

Table 44 indicates some of the aromatic compounds isolated after exposing kerosene to seawater. Such detailed breakdowns of hydrocarbons are rarely performed, and even this particular one is incomplete. In addition these specific compounds are not necessarily present in all kerosenes. The exact composition depends on the types and composition of the crude oil feedstock, the refinery processes employed, and the components used in product blending. This is true for all the petroleum products. The large number of individual hydrocarbon compounds precludes the identification and consideration of each one separately. Further assessments of the toxicity of particular products should concentrate on the identification of aromatic compounds present, particularly those with high volatility and solubility.

In general the content of low molecular weight aromatics (which are usually more volatile and soluble) in refined products is greater than in crude oils because refining may include thermal and catalytic cracking in addition to distillation. Cracking yields a blending component which has a higher aromatic content than the original feedstock. Because of this higher aromatic content, petroleum products are often more toxic than many crude oils. Light and middle distillates almost always are more toxic to marine life than most crude oils. Table 45 indicates the levels of aromatics capable to causing harmful effects to marine organisms and the quantities of #2 fuel oil and crude oil which contain these toxic levels of aromatics. It is evident that even fuel oils are more toxic than crude oils. However, volatiles in some crude oils may be 20-30 percent of their volumes, whereas often only one percent of Bunker C fuel oil contains volatile hydrocarbons; thus the crude oils would tend to have a greater direct toxicity.

Petroleum products themselves have different relative toxicities. Liquefied petroleum gases, gasoline, jet fuel, and kerosene are often composed totally of volatile hydrocarbons which evaporate rapidly upon exposure to seawater. More than 75 percent of the hydrocarbons in distillate fuels frequently will evaporate within a few days. Heavier products, including asphalt and Bunker C fuel oil, often contain less than 10 percent volatile hydrocarbons

Table 43

Relative Percentages of Hydrocarbon Compounds in Petroleum Products Transported in Puget Sound

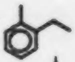
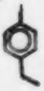
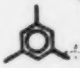
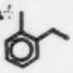
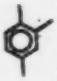
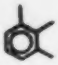
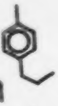
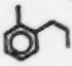
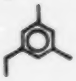
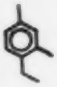
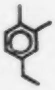
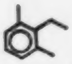
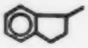
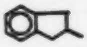
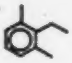
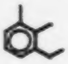
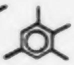
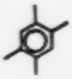
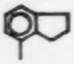
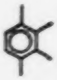
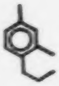
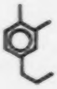
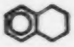
Petroleum Product	Paraffins	Naphthenes	Aromatics
LPG	100	0	0
Motor Gasoline	40-50	30-40	10-35
Jet Fuel	35	50	15
Kerosene	40	45	15
Distillate Fuel Oils	30	45	25-40
Residual Fuel Oils§	15	45	25
Naphtha, Petroleum Solvents	20-35	30-45	20-50
Lubricating Oils & Greases	20-40	30-55	15-45
Asphalt	---	---	---

§ includes 15% non-hydrocarbon compounds containing oxygen, nitrogen or sulfur.

NOTE: Olefins are often not measured, although they are present in most products to some degree.

Table 44

Some Soluble Aromatic Compounds Isolated from Kerosene

COMPOUND		C B.PT.	PEAK #	CONC. (µG/L)
BENZENES				
1-METHYL-2-ETHYL BENZENE		161.3	2	6.68
1-METHYL-4-ETHYL BENZENE		161.99	2	
1:3:5-TRIMETHYL BENZENE		164.72	3	8.10
1-METHYL-2-ETHYL BENZENE		165.15	3	
1:2:4-TRIMETHYL BENZENE		169.35	4	20.15
1:2:3-TRIMETHYL BENZENE		176.08	5	18.07
			6	
1-METHYL-4-PROPYL BENZENE		183.30	7	5.93
1-METHYL-2-PROPYL BENZENE		184.80	7	
1:3-DIMETHYL-5-ETHYL BENZENE		183.58	7	
1:3-DIMETHYL-4-ETHYL BENZENE		188.20	8	18.17
1:2-DIMETHYL-4-ETHYL BENZENE		189.40	8	
1:3-DIMETHYL-2-ETHYL BENZENE		190.01	8	
1-METHYLINDANE		190.6	8	
2-METHYLINDANE		191.4	8	
1:3-DIMETHYL-2-ETHYL BENZENE		190.1	8	
1:2-DIMETHYL-3-ETHYL BENZENE		193.91	9	6.21
1:2:3:5-TETRAMETHYL BENZENE		198.00	10	16.57
1:2:4:5-TETRAMETHYL BENZENE		196.80	10	
4-METHYL INDANE		205.5	11	35.39
1:2:3:4-TETRAMETHYL BENZENE		205.04	11	
1:3-DIMETHYL-4-PROPYL BENZENE		206.6	11	
1:2-DIMETHYL-4-PROPYL BENZENE		208.5	11	
TETRAHYDRONAPTHALENE		207.57	11	

Source: (13)

Table 44 (cont.)

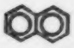
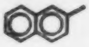
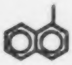
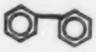
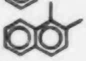
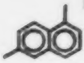
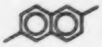
NAPTHALENES				
NAPTHALENE		217.96	12	152.89
2-METHYL NAPTHALENE		241.05	13	85.66
1-METHYL NAPTHALENE		244.64	14	63.43
BIPHENYL		255.2	15	27.49
1:2-DIMETHYL NAPTHALENE			16	32.95
1:6-DIMETHYL NAPTHALENE			16	
2:6-DIMETHYL NAPTHALENE		262	16	
TOTAL AROMATICS				610

Table 45

Summary of Aromatic Toxicity Data

CLASS OF ORGANISM	ESTIMATED CONCENTRATION (ppm) OF SOLUBLE AROMATICS CAUSING TOXICITY	ESTIMATED AMOUNT (ppm) OF PETROLEUM SUBSTANCES CONTAINING EQUIVALENT AMOUNT OF AROMATICS	
		#2 FUEL OIL	FRESH CRUDE
FLORA	10-100	50-500	10^4-10^5
GASTROPODS (SNAILS, etc.)	10-100	50-500	10^4-10^5
FINFISH	5-50	25-250	10^4-10^5
BIVALVES (OYSTERS, CLAMS, etc.)	5-50	25-250	10^4-10^5
PELAGIC CRUSTACEANS	1-10	5-50	10^3-10^4
BENTHIC CRUSTACEANS (LOBSTERS, CRABS, etc.)	1-10	5-50	10^3-10^4
OTHER BENTHIC INVERTEBRATES (WORMS, etc.)	1-10	5-50	10^3-10^4
LARVAE (ALL SPECIES)	0.1-1.0	0.5-5	10^2-10^3

Source: (14)

which will be evaporated by weathering processes. Thus on the basis of volatile hydrocarbon content alone, gasoline and other light products will usually be more toxic than heavier products. However, examination of the classes of hydrocarbon compounds present is more important. Liquefied petroleum gas is essentially 100 percent paraffinic. This high content of volatile paraffins may be toxic to marine organisms. However, other refined products, containing aromatic compounds, have more soluble toxic hydrocarbons and will have a longer period of exposure in the marine environment. Distillate fuel oils usually have the greatest average aromatic content, followed by some motor gasolines and jet fuels. Thus, on the basis of aromatic content, these products are probably the most toxic. Closer examination provides evidence that #2 fuel oil has a greater amount of volatile, soluble aromatic hydrocarbons than the other petroleum products. Ranking the remaining products is difficult due to the interplay of the main factors determining toxicity; aromatic content, solubility and volatility.

Another significant factor controlling the lethal effects of refined products is the effect of weathering. Evaporation acts fairly rapidly on the volatile fractions of a spilled petroleum product. The interactions of dissolution and evaporation will determine how much exposure to toxic hydrocarbon compounds marine organisms will have. For many of the products, particularly the light distillate products, a large percentage of toxic components are lost within two to four days after spillage. Mortality rates from direct lethal toxicity are lessened as the products are weathered. Still, as indicated previously in Table 45, very low concentrations of soluble aromatic hydrocarbons may cause lethal effects to marine organisms. Larval stages appear to be considerably more sensitive than adults. Concentration of soluble aromatics below 0.1 ppm may be toxic to certain marine larvae. In general, crustaceans and burrowing animals are the most sensitive to refined products; fish and bivalves are moderately sensitive, and gastropods and plants are the least sensitive.

While #2 fuel oil has the greatest short-term effect on marine life, causing high rates of direct mortality and sublethal effects, #6 fuel oil, Bunker C, probably has the greatest long-term effect, particularly regarding coating of organisms and changes in marine habitats. Light aromatic hydrocarbons will be evaporated or enter into solution fairly rapidly. The high molecular weight aromatics are less soluble and less volatile and will remain unchanged for a long period of time. Crude oils, particularly heavy ones, also have long-term direct and indirect lethal effects. In general, the coating and smothering of organisms by crude oil and heavy products is a major cause of mortality only after the toxic soluble aromatic hydrocarbons have evaporated. The organisms most susceptible to coating are those organisms unable to leave the area in which the oil is spilled. Heavy products like Bunker C may also drastically alter the marine habitat once the oil is incorporated into the sediments. The amount of product that gets into the sediments is a function of the particle size distribution in the sediment, the strength of vertical mixing, the water depth and, the extent to which the product has weathered.

Further assessment and characterization of the toxic components of petroleum products in the future is necessary to better define the particular compounds which occur in products and cause harmful effects. These efforts should be directed primarily at analyzing the aromatic hydrocarbons present in refined products, particularly soluble naphthalene aromatic compounds. Attempts at a complete tabulation of hydrocarbon compounds present in individual petroleum products are difficult and may be comparatively meaningless due to wide variations in product constituency. Instead, characterizations should include information on the relative percentages of aromatics, percentages of volatiles and volatile aromatics, and solubilities for benzene and naphthalene aromatic hydrocarbons.

D. Refinery Processes

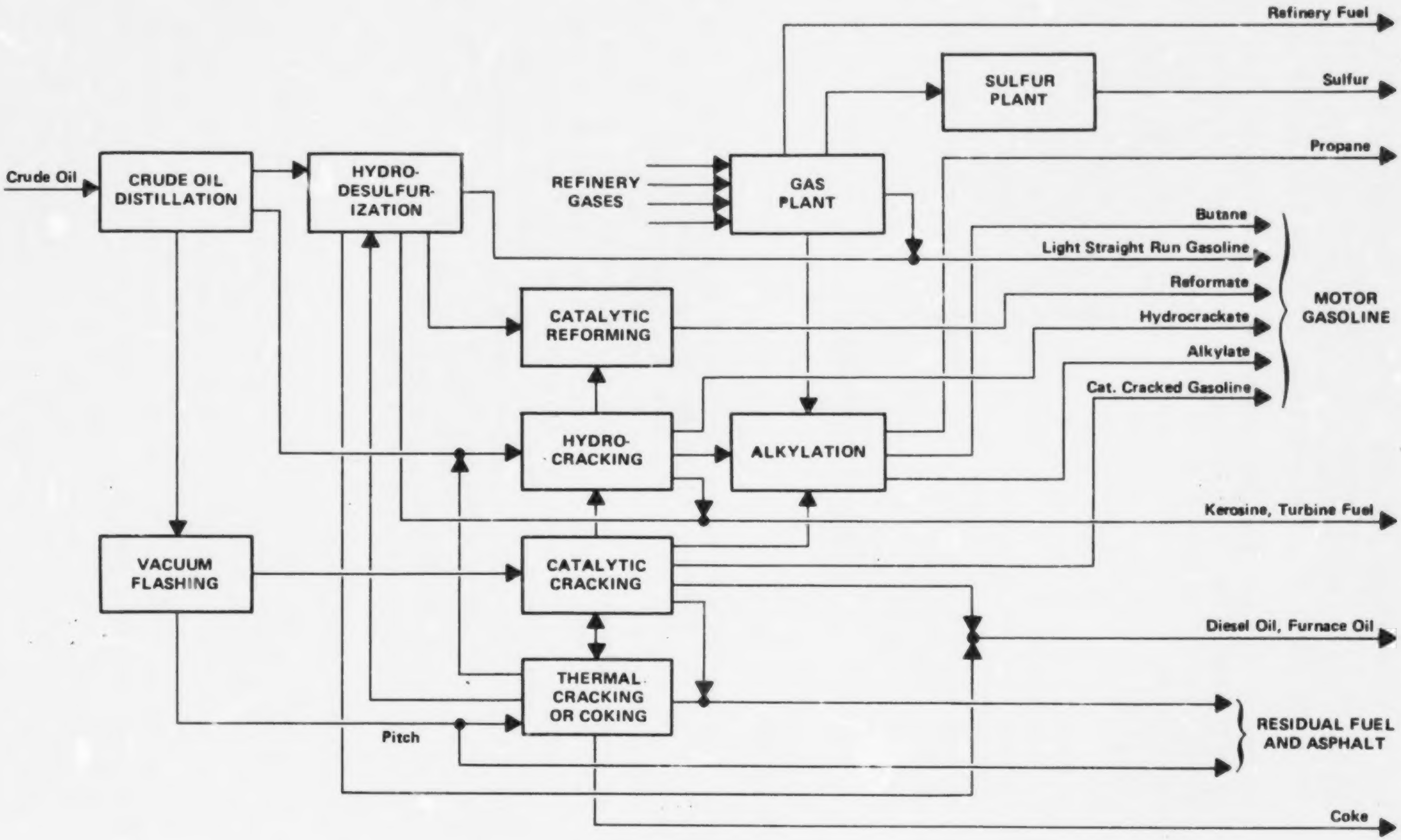
1. Introduction

The six refineries located on Puget Sound in Washington are very representative of the diversity which can be found among petroleum refineries, while concurrently they share numerous commonalities. The actual process configuration of an individual refinery will depend on the range and type of products desired and the sources and types of available crude oils for feedstock. When these considerations have been made, a number of different processes for treating the crude must be examined regarding their functions and capabilities. Then a decision as to the refinery design can be reached. Some of the major processes available for consideration are: crude desalting, atmospheric distillation, vacuum fractionation, thermal cracking, catalytic cracking, hydrocracking, polymerization, alkylation, isomerization, catalytic reforming, hydrotreating and product blending. A simplified refinery process diagram is shown in Figure 8.

2. General Process Description

a. Crude Desalting. When crude oil is taken from the ground it contains much water and salts, along with the oil, which are detrimental to most refining processes. Removal of this salty water is called crude desalting. Two basic methods of desalting are available, one involving gravity separation and the other an electrostatic field. In the first method chemical emulsifiers which will remove the specific types of salt present are added with the wash water. The mixture is heated while the emulsifier separates the salty water from the crude oil. A settling tank allows gravity separation of the crude and water, and the desalted crude is withdrawn from the upper portion of the tank. The other major method utilizes an electrostatic field to separate

Figure 8 Simplified Modern Refinery Process Flow Diagram


Crude Oil
CRUDE OIL DISTILLATION
HYDRO-DESULFUR-IZATION
REFINERY GASES
GAS PLANT
SULFUR PLANT
CATALYTIC REFORMING
HYDRO-CRACKING
ALKYLATION
VACUUM FLASHING
CATALYTIC CRACKING
THERMAL CRACKING OR COKING
Pitch
Refinery Fuel
Sulfur
Propane
Butane
Light Straight Run Gasoline
Reformate
Hydrocrackate
Alkylate
Cat. Cracked Gasoline
MOTOR GASOLINE
Kerosine, Turbine Fuel
Diesel Oil, Furnace Oil
RESIDUAL FUEL AND ASPHALT
Coke

Source: (16)

Reprinted with permission from: Environmental Conservation; The Oil and Gas Industries, 1972. National Petroleum Council, Washington, D.C. Vol. 2.

the crude and salty wash water, instead of gravity separation. The influence of the high voltage field causes the dispersed droplets to agglomerate, aiding separation. The contaminated wash water is discharged into the wastewater stream and the relatively clean, desalted crude is withdrawn to the fractionation facilities.

b. Crude Fractionation. The rest of the crude unit in a refinery consists of fractionation and distillation apparatus. Fractionation separates the various fractions of the crude oil into several specified classes, according to boiling point ranges. This separation is necessary to allow further treatment in the refinery to produce the desired products. Atmospheric distillation and vacuum fractionation are the two most common methods, and are often employed in series. Atmospheric distillation involves heating the crude up to around 650°F. As the various intermediate fractions reach their boiling points, they tend to rise in the distillation tower. The lightest products (C_5 and lighter) will rise to the top of the tower. The rest of the distilled fractions; gasoline, kerosene, naphtha and diesel separate according to boiling point ranges and are drawn off from the tower by sidestreams at the appropriate height. The residual crude oil is removed from the bottom of the tower. This heavy material serves as feedstock for vacuum fractionation or flashing. Again heat is applied; often the temperature in this unit is above 900°F. Separation occurs under low pressure in the unit, yielding light and heavy vacuum oil for catalytic cracking feedstock and a residuum fraction. Some refineries use a barometric condenser to create the reduced pressures in the vacuum unit, although surface condensers are more common, especially in large refineries. The heavy residuum may receive a number of different treatments, including delayed coking, catalytic cracking and deasphalting. Often the deasphalting unit is found within the crude unit, whereas the other treatments are major processes. Deasphalting uses propane or butane to further separate the crude by extraction and yields two streams: deasphalted oil and petroleum asphalt.

c. Cracking Processes. There are three types of cracking processes: thermal cracking, catalytic cracking and hydrocracking. The purpose of these processes is to take distillate fractions heavier than naphtha and "crack" them, producing lighter distillates, particularly gasoline and naphtha.

   i. Thermal Cracking. This category includes visbreaking and delayed coking as well as regular thermal cracking. In each of these operations, heavy fractions from the vacuum fractionation unit or the catalytic cracker are broken down into lower molecular weight fractions utilizing heat, but no chemical catalyst. Typical conditions found with thermal cracking operations are temperatures of 900°-1100°F and pressures of 40-70 atm. This process yields some lighter blending stocks, feedstock for other cracking units and a very heavy residue used for bunker fuels and heavy fuel oils. Thermal cracking processes are gradually being phased out as catalytic cracking and hydrocracking gain predominance, largely for economic and efficiency reasons.

ii. Catalytic Cracking. Catalytic cracking also breaks heavy fractions, usually from the vacuum fractionator, into lower molecular weight fractions. This is probably the most important process in the production of high-octane gasoline stocks. The use of a catalyst allows cracking operations at lower pressures and temperatures than thermal cracking processes. It also inhibits the formation of undesirable polymerized products. Catalytic crackers may be fluid catalytic cracking (FCC) units or Thermofor catalytic cracking (TCC) units. Fluid catalytic crackers utilize a finely powdered catalyst which is handled as an aerated "fluid" and is easily circulated by pressure differentials in the unit. Thermofor catalytic crackers use the catalyst in the form of small spheres - the bead catalyst. These small beads are well suited for circulation by low air pressure, which raises the regenerated catalyst to a hopper above the reactor.

A catalytic cracking unit is composed of three sections - cracking, regeneration and fractionation. Regenerated catalyst is constantly being supplied to the cracking reactor, while spent catalyst is being continually removed to the regenerator. The hot spent catalyst contains a deposit of coke which must be removed in order to restore the activity of the catalyst. The coke is burned off with air and the regenerated catalyst, passing out of the regenerator, is mixed with the oil feed and returns to the reactor. The oil is cracked in the reactor, the vapor passes upward, and then through a fractionating column, where the desired fractions are drawn off. With fluid catalytic crackers a portion of the bottoms of the fractionating tower must be passed through a settler to remove small amounts of fine catalyst. This is not a problem with a Thermofor catalytic cracker. The small catalyst beads are handled differently and there is less tendency for catalyst entrainment. Operating conditions are also slightly different; the temperatures in a fluid catalytic cracker are normally 1050° to 1125°F, while they are only 840° to 920°F in a Thermofor catalytic cracking unit.

iii. Hydrocracking. This process is basically the same as catalytic cracking, except that it is performed in the presence of hydrogen, at lower temperatures (400°-800°F) and higher pressures. Hydrocracking offers a greater flexibility, cleaner products and reduced formation of olefins.

d. Polymerization. Polymerization units are used to convert olefin feedstocks (primarily propylene) into high octane rating polymer units. The polymerization unit generally consists of a feed treatment unit (applying heat and removing sulfides, mercaptans and nitrogen compounds), a catalytic reactor, an acid removal section and a gas stabilizer. The feedstock, rich in olefins, is passed through the feed treatment unit and is brought up to reaction temperature. It passes through the reactor at 300°-425°F and goes to fractionating equipment. There it is first depropanized, then debutanized and the polymer product is drawn off from the bottom of the fractionator. The catalyst employed is usually phosphoric acid, although sulfuric acid is used in some older units. The catalyst is recovered in the acid removal section and regenerated for reuse in the reactor. Polymerization is actually only a marginal process since the product octane rating is not too much higher than other gasoline blending stocks. Thus, there is a downward trend in employing this process in new refineries.

e. Alkylation. Alkylation involves the reaction of an olefin (propylene, butylene, amylene) and an isoparaffin (usually isobutane) in the presence of a catalyst at controlled temperatures and pressure to produce a high octane alkylate as a gasoline blending stock. Sulfuric acid is the most widely used catalyst, although hydrofluoric acid is also used. The isobutane and olefin feedstock are mixed in the reactor which contains strong sulfuric acid. An acid hydrocarbon emulsion is formed, part of which is recycled to the reactor along with fresh feedstock. The remaining emulsion flows into a settling chamber where the acid separates out. Part of the acid is recycled and the rest is discarded. The hydrocarbon product is washed with caustic and water and fractionated. The fractionation yields isobutane (for recycling), normal butane and alkylate. This process may have increasing importance as the demand for low lead, high octane gasoline increases.

f. Isomerization. This process is used to obtain higher octane motor fuel by converting light gasoline stocks into their higher octane isomers. The greatest application of this technique has been in the conversion of normal butane to isobutane, for use as a feedstock for the alkylation process. Liquid normal butane is passed through a drying tower and vaporized. The vapor is passed to a reactor, where, in the presence of a catalyst (usually aluminum chloride) nearly 40 percent becomes isobutane. The vapor is stripped from the catalyst and fractionated, with the unconverted normal butane being recycled.

g. Catalytic Reforming. Reforming converts low octane naphtha, heavy gasoline and naphthene-rich stocks to high octane gasoline blending stock that is high in aromatics. Hydrogen is a significant by-product of the process. The predominant reaction during catalytic reforming is the dehydrogenation of naphthenes.

Secondary reactions which are also important are the isomerization and dehydrocyclization of paraffins. All three of these reactions result in higher octane products. The feedstocks are usually hydrotreated to remove sulfur and nitrogen compounds that would poison the catalyst. The vaporized feedstock is passed through a reactor containing the catalyst and then is cooled. Next it is released to a gas separator, where hydrogen is removed, then passed to a stabilizer from which the final product is withdrawn.

h. Hydrotreating. Hydrotreating processes are used to saturate olefins, and to remove sulfur and nitrogen compounds. Hydrotreating processes are used to reduce the sulfur content of product streams from sour crudes by 90 percent while nitrogen is reduced by 80 to 90 percent. Generally the feedstock is mixed with hydrogen, heated and charged to the catalytic reactor. The reactor products are cooled and the hydrogen, impurities and high grade product are separated out. The primary variables influencing hydrotreating are the type of catalyst, hydrogen partial pressure, process temperature and contact time. Hydrotreating is commonly applied to catalytic reformer feedstock, catalytic cracking feedstock and for desulfurization of naphtha, heavy gas oil and residuals. Hydrorefining and hydrofinishing are very similar to hydrotreating. Each provides desulfurization with hydrogen, to varying degrees. Hydrofinishing is the least extensive treatment, with hydrorefining providing a middle range of treatment. Which level of treatment utilized will depend on the types of crudes being used and the desired cleanliness of the products.

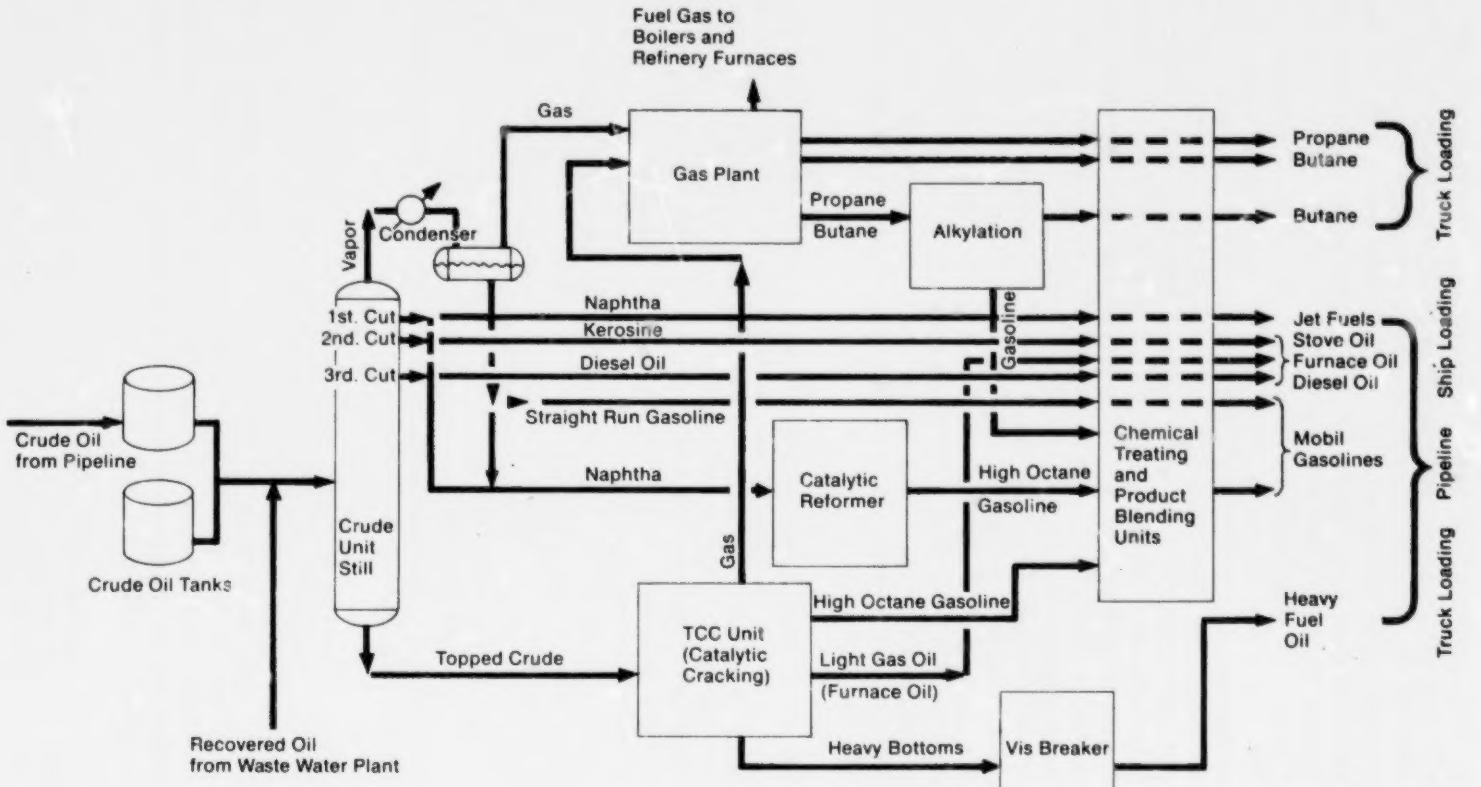
i. Product Finishing. Blending is the final step in producing finished products to meet market demands and quality specifications. The largest operations involve blending the various gasoline stocks and additives (including anti-knock and anti-icing compounds). Diesel fuels and other products also involve blending of components and additives. This process is usually highly automated and is often controlled by computer.

3. Process Configurations for Puget Sound Refineries

a. Mobil. Since 1955 when the Mobil refinery went into operation, an almost continuous expansion has taken place to modernize the plant and maintain a high degree of process efficiency. The major processes and processing units utilized at the refinery are: crude desalting, atmospheric distillation, vacuum fractionation, Thermofor catalytic cracking, catalytic reforming, visbreaking, polymerization, alkylation, hydrofinishing, chemical treating and product blending (Figure 9). The refinery was designed primarily to handle light, sweet crudes and therefore has no sulfur recovery plant at the present time. To meet the possibility of utilizing crude oils with a higher sulfur content and to reduce sulfur levels in emissions, a sulfur recovery unit is being constructed, and is expected to be in operation by early 1977.

Figure 9

Refinery Process Configuration at the Mobil Refinery


Fuel Gas to
Boilers and
Refinery Furnaces
Gas
Gas Plant
Propane
Butane
Alkylation
Propane
Butane
Butane
Truck Loading
Vapor
Condenser
1st. Cut
2nd. Cut
3rd. Cut
Naphtha
Kerosine
Diesel Oil
Straight Run Gasoline
Naphtha
Gasoline
Jet Fuels
Stove Oil
Furnace Oil
Diesel Oil
Ship Loading
Crude Oil
from Pipeline
Crude Oil Tanks
Crude
Unit
Still
Catalytic
Reformer
High Octane
Gasoline
Chemical
Treating
and
Product
Blending
Units
Mobil
Gasolines
Pipeline
Gas
TCC Unit
(Catalytic
Cracking)
High Octane Gasoline
Light Gas Oil
(Furnace Oil)
Heavy
Fuel
Oil
Truck Loading
Topped Crude
Recovered Oil
from Waste Water Plant
Heavy Bottoms
Vis Breaker

Source: (20)

As with most refineries the crude oil is first pumped to the electrostatic crude desalting unit where the salts present are removed to prevent corrosion and to produce a cleaner feedstock for the main process units. The crude passes on to the atmospheric distillation unit where it is heated under pressure, then released into the low pressure distillation tower. In the tower the oil is separated by boiling point into different fractions. The light end products rise to the top of the tower and are withdrawn for additional fractionation in the gas plant. Some of this fraction condenses in a condenser as straight run gasoline and goes directly to the chemical treating and blending units. Also the next three fractions in the distillation tower, naphtha, kerosene and diesel oil, are withdrawn and blended, and receive chemical treating. A portion of the naphtha fraction from the tower passes on to the catalytic reformer. The heaviest fractions are withdrawn from the tower to a tar separator, then are broken down further in the vacuum fractionation unit. The output from the vacuum unit is charged directly to the Thermofor catalytic cracker (TCC). Here, in the presence of a catalyst and high temperatures, the heavy fraction is broken down into four major fractions: gases, high octane gasoline, light gas oil and residual oil.

The gases go to the gas plant where propane and heavier gases are recovered. These pass on to the alkylation unit or are sold. Gases lighter than propane are used as fuel gas for the boilers and furnaces at the refineries. The light gas oil receives chemical treatment and is blended to yield furnace oil. The high octane gasoline from the TCC unit is blended with other gasoline streams for production of three grades of Mobil motor gasoline. The heavy residual oil can be heated to high temperatures at high pressure in the visbreaker. This would convert it to heavy fuel oil for use in industrial power generation plants and as bunker fuel for ships. However, the energy cost of operating this visbreaker versus the actual improvement in quality of the heavy oils has not proved to be economical for Mobil. So, since 1972, this process has not been utilized and the heavy residual oil is sold as Bunker C fuel.

The catalytic reformer, also known as a Sovaformer, receives middle fractions of naphtha from the crude unit as feedstock and produces high octane reformate for gasoline blending, turbine fuels and heating oil. This occurs at high temperature and pressure in the presence of a bimetallic catalyst. A portion of the feedstock undergoes hydrofinishing to remove mercaptans and other sulfur compounds which could reduce the efficiency of the catalytic reformer.

The alkylation unit receives the propane-butane fraction from the gas plant and converts it in part to a high octane ingredient. This alkylate is blended with the other gasoline streams to produce motor gasolines. A polymerization unit is also available but it is a marginal process because the product octane is not significantly higher than the other gasoline blending stocks and so does not provide much upgrading of the overall motor fuel pool. Alkylation produces a high octane alkylate and has a higher yield per unit of feedstock than does polymerization. So at Mobil, the polymerization unit is only used when the alkylation unit is shut down for maintenance or repair. Besides yielding high octane alkylate, the alkylation unit produces some butane, which is reused.

Additives are blended into the three gasoline grades to provide higher performance for the motorist. Among them are compounds that maintain the quality of gasoline in storage, inhibit rust, assure uniform combustion and clean vital engine parts.

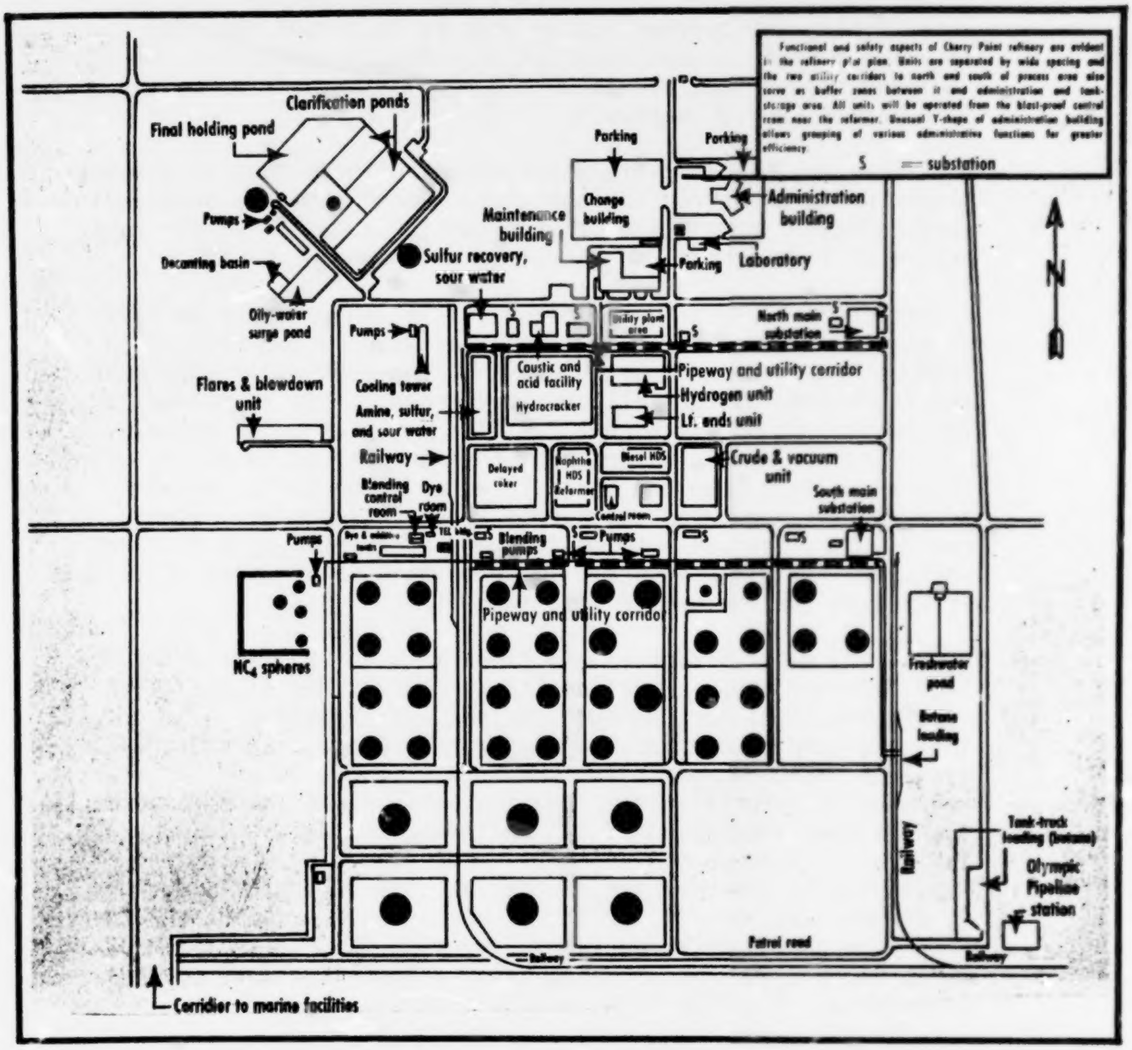
A portion of the wastewater generated in the refinery receives in-plant treatment. Desalter effluent waters, polymerization feed wash waters and sour waters from the overhead accumulator and knockout drums are all steam stripped. This is primarily for removal of sulfides, but may also strip ammonia, phenols, and cyanide. Bottom waters from the stripper go to an API separator, then into the phenolic water surge tank. Gases produced are condensed and burned in an incinerator. Spent caustic is stored in a surge tank and is treated by a flue-gas stripper. The stripped and diluted caustic solution is continuously bled to the wastewater treatment plant.

b. ARCO. The major processes and processing units utilized at the ARCO refinery are: crude desalting, atmospheric distillation, vacuum fractionation, delayed coking, hydrotreating, hydrocracking, hydrogen production, catalytic reforming, chemical treating, gasoline blending and sulfur recovery (Figures 10 and 11). The refinery is very different from the other Puget Sound refineries and was specifically built to handle Alaskan North Slope crudes. It is an "all-hydrogen" refinery, with all process streams being substantially hydrotreated, producing cleaner products. There is a great deal of flexibility of operations, allowing the refinery to run other crude types, prior to the availability of North Slope crude, while maintaining a high degree of process integration, yielding high quality products.

Initially the crude is washed to remove salt and prevent corrosion, then is heated to its boiling point in the atmospheric distillation towers. The light end products are drawn off the light end unit. The naphtha fractions are withdrawn and are hydrotreated prior to being reformed. Fractions in the general range of 390°-525°F are withdrawn directly to the chemical treating unit. Potential jet fuel fractions are removed and hydrotreated. The heaviest hydrocarbon fraction, the gas oils, passes on to the vacuum fractionation unit, for further breakdown. After additional treatment, a portion of the stream from the vacuum unit goes to the hydrocracker and the residuum goes to the delayed coker.

Figure 10

Diagram of the Layout of the ARCO Refinery at Cherry Point


Final holding pond
Clarification ponds
Pumps
Decanting basin
Oily-water surge pond
Sulfur recovery, sour water
Flares & blowdown unit
Pumps
Cooling tower
Amine, sulfur, and sour water
Railway
Blending control room
Dye room
Dye & additive tanks
TEL bldg.
Parking
Change building
Maintenance building
Parking
Administration building
Parking
Laboratory
S
Utility plant area
North main substation
Caustic and acid facility
Hydrocracker
Pipeway and utility corridor
Hydrogen unit
Lt. ends unit
Delayed coker
Naphtha HDS Reformer
Diesel HDS
Control room
Crude & vacuum unit
South main substation
Pumps
Blending pumps
Pumps
Pipeway and utility corridor
NC_4 spheres
Freshwater pond
Butane loading
Railway
Tank-truck loading (butane)
Olympic Pipeline station
Patrol road
Railway
Railway
Corridor to marine facilities
N

Functional and safety aspects of Cherry Point refinery are evident in the refinery plot plan. Units are separated by wide spacing and the two utility corridors to north and south of process area also serve as buffer zones between it and administration and tank-storage area. All units will be operated from the blast-proof control room near the reformer. Unusual Y-shape of administration building allows grouping of various administrative functions for greater efficiency.

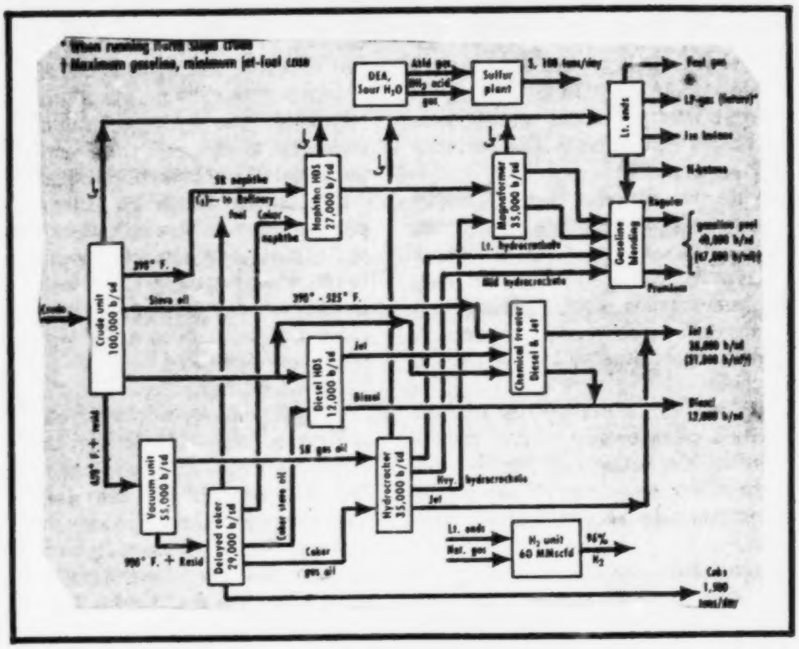
S = substation

Source: (1)

Reprinted with permission from:
Aalund, Leo, 1972. "Cherry Point Refinery",
Oil and Gas Journal, Vol. 70, No. 4. 65-72

Figure 11

Refinery Process Configuration at the ARCO Refinery


* When running North Slope crude
† Maximum gasoline, minimum jet-fuel case
DEA, Sour H_2O
Acid gas
NH_3 acid gas
Sulfur plant
S, 100 tons/day
Lt. ends
Fuel gas
LP-gas (butane)*
Iso butane
N-butane
Naphtha HDS 27,000 b/sd
SR naphtha
(s)— to Refinery fuel
Coker naphtha
Magnaformer 35,000 b/sd
Gasoline blending
Regular
Premium
gasoline pool 48,000 b/sd (67,000 b/sd†)
Crude
Crude unit 100,000 b/sd
390° F.
Stove oil
390° - 525° F.
Lt. hydrocrackate
Mid hydrocrackate
Diesel HDS 12,000 b/sd
Jet
Diesel
Chemical treater Diesel & Jet
Jet A 38,000 b/sd (31,000 b/sd†)
Diesel 12,000 b/sd
650° F.+ resid
Vacuum unit 55,000 b/sd
SR gas oil
Hydrocracker 35,000 b/sd
Hvy. hydrocrackate
Jet
Coker stove oil
Delayed coker 29,000 b/sd
950° F. + Resid
Coker gas oil
Lt. ends
Nat. gas
H_2 unit 60 MMscfd
96% H_2
Coke 1,500 tons/day

Source: (1)

Reprinted with permission from:
Aalund, Leo, 1972. "Cherry Point Refinery",
Oil and Gas Journal, Vol. 70, No. 4. 65-72

The residuum is heated and injected into the four available coke drums to be cracked down to lighter molecules. The light hydrocarbons formed in the delayed coker pass on to the naphtha hydrotreater, the diesel hydrotreater and the hydrocracker. The solid residue of carbon, called coke, is removed from the drums, crushed and loaded into railroad cars for shipment to Japan. The two hydrotreating units, receiving fractions from the distillation unit and the delayed coker, use hydrogen to remove sulfur compounds from the crude. These units and the hydrocracker and sour water strippers remove 97 percent of all the sulfur compounds present. In the sulfur recovery plant these compounds are converted to pure sulfur by two parallel units. The sulfur is stored above ground in storage tanks in a liquid form prior to being sold.

The four hydrocracker reactors receive streams of gas oil from the vacuum fractionation unit and the delayed coker. These large hydrocarbon compounds are broken down, or cracked, to lighter compounds for later blending of jet fuels and gasoline. Hydrogen is combined with the cracked molecules while under high pressure and in the presence of a catalyst, providing hydrotreating of the streams and providing cleaner products. The cracked products are separated into fractions and then pass on to various parts of the plant. The light and middle hydrocrackate fractions are kept separate but are made available for gasoline blending. The heavy hydrocrackate is shunted to the catalytic reforming unit. The jet fraction joins the chemically treated straight run and hydrotreated jet fractions from the crude unit and the diesel hydrotreating unit to yield top quality Jet-A fuel. The light ends from the hydrocracker, along with light fractions from the catalytic reformer, furnishes the feed for the hydrogen unit, which in turn supplies the diesel and naphtha hydrotreating units, the catalytic reformer and the hydrocracker with hydrogen.

The catalytic reforming unit, also called a magnaformer, has three radial and one spherical reactors, a fairly recent innovation in catalytic reformer design. Here, the low octane gasoline from the distillation tower, the delayed coker and hydrocracker is processed to yield high octane gasoline. Although the magnaformer is designed to utilize a platinum/rhenium catalyst when North Slope crudes are being reformed, presently a conventional noble-metal catalyst is being used. Under high temperature and pressure, and the influence of the catalyst, the molecules are rearranged, providing a high octane reformate available as a blending component for low lead and no-lead gasolines. The reformate is separated into two fractions which are blended in the gasoline blending unit with light and middle hydrocrackate and a butane stream from the light ends unit, yielding a variety of motor gasolines.

Diesel fuel and some light end products are the only other products produced at Cherry Point. The diesel fuel is of fairly high quality and is sold as motor diesel fuel. The process arrangement allows for the option of making some bunker fuels but no fuel oils. The light ends unit yields butane, some of which goes for gasoline blending and fuel gas. The fuel gas is composed of propane and lighter gases, although in the future, propane may be recovered and sold on the liquefied petroleum gas market.

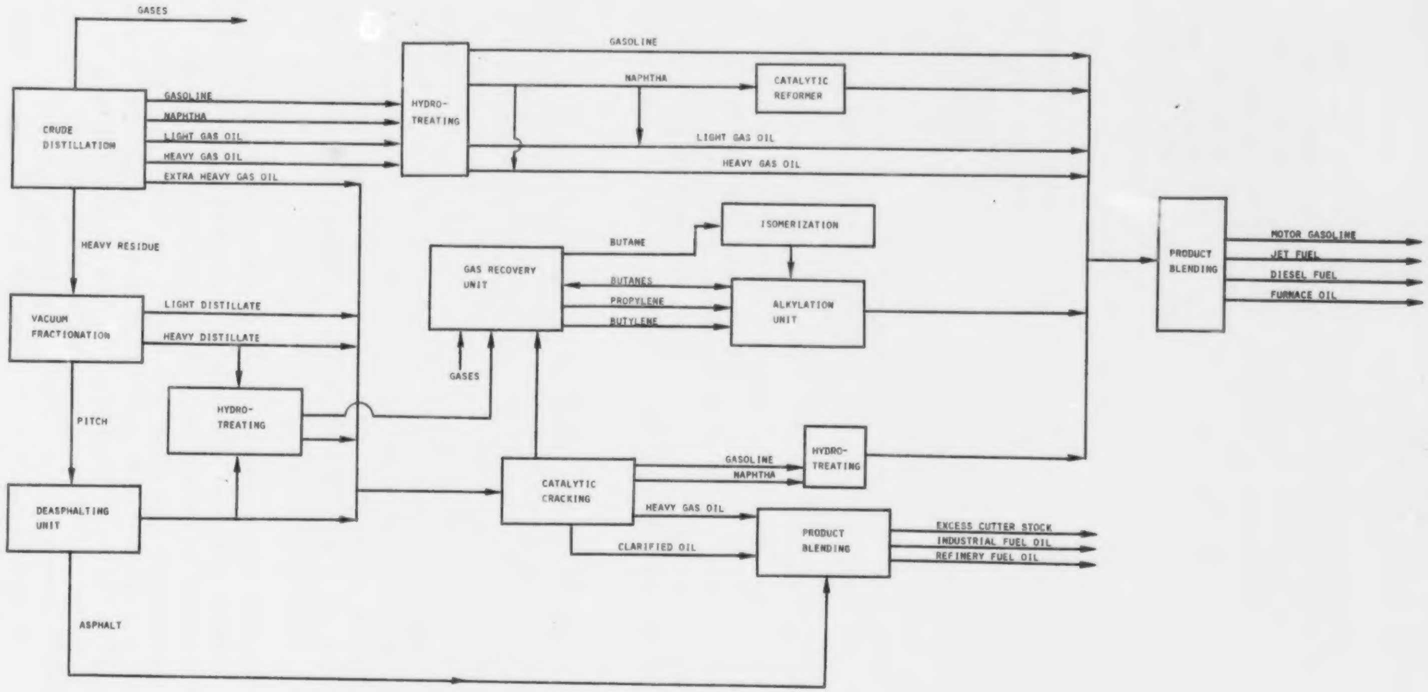
Water use in the refinery and its processes has been minimized wherever possible. Boiler blowdown has been reduced by demineralizing the boiler feedwater. Sour water, from the crude-vacuum unit, naphtha and diesel hydrotreating units, the hydrocracker and the delayed coker, are all treated prior to discharge to the wastewater treatment plant. This in-plant facility removes hydrogen sulfide, ammonia and small amounts of mercaptans, and separates dissolved and suspended oil. The sour water is steam stripped and the H_2S and NH_3 removed passes on to the sulfur recovery plant. Phenolic water is also fed to a steam stripper, but is kept separate so that the water can be used as desalter water in the crude desalting unit, for further removal of phenols. Waste acids and caustic solutions also receive in-plant pretreatment and are neutralized before being released to the waste treatment plant.

c. Shell. The Shell refinery employs the following processes and processing units: crude desalting, atmospheric distillation, vacuum fractionation, deasphalting, hydrotreating, catalytic cracking, catalytic reformer, gas recovery plant, butane isomerization, alkylation, caustic treating and products blending (Figure 12). Crude oil received from tankers and crude pipeline first is treated in the crude desalter, then passes on to the atmospheric distillation tower. Here, the crude is fractionated into a number of streams each receiving varying degrees of treatment.

The lightest gases are withdrawn and used for refinery fuel gas. Butane goes to the butane isomerization unit where normal butane is converted to isobutane for the alkylation unit. Straight run gasoline receives chemical treating and becomes a blending component for motor gasoline. Some low octane straight run naphtha and the light gas oil fraction receive hydrotreating in separate units and are blended for aviation turbine (jet) fuel. The heavy gas oil fraction is chemically treated and blended with hydrotreated naphtha to produce furnace oil. The majority of the hydrotreated naphtha passes on to the catalytic reformer where the octane is raised. The high octane reformate is used as a gasoline blending stock.

Figure 12

Refinery Process Configuration at the Shell Refinery



GASES
CRUDE DISTILLATION
GASOLINE
NAPHTHA
LIGHT GAS OIL
HEAVY GAS OIL
EXTRA HEAVY GAS OIL
HYDRO-TREATING
GASOLINE
NAPHTHA
CATALYTIC REFORMER
LIGHT GAS OIL
HEAVY GAS OIL
HEAVY RESIDUE
ISOMERIZATION
BUTANE
GAS RECOVERY UNIT
BUTANES
PROPYLENE
BUTYLENE
ALKYLATION UNIT
PRODUCT BLENDING
MOTOR GASOLINE
JET FUEL
DIESEL FUEL
FURNACE OIL
VACUUM FRACTIONATION
LIGHT DISTILLATE
HEAVY DISTILLATE
GASES
PITCH
HYDRO-TREATING
CATALYTIC CRACKING
GASOLINE
NAPHTHA
HYDRO-TREATING
DEASPHALTING UNIT
HEAVY GAS OIL
CLARIFIED OIL
PRODUCT BLENDING
EXCESS CUTTER STOCK
INDUSTRIAL FUEL OIL
REFINERY FUEL OIL
ASPHALT

The extra heavy gas oil cut from the distillation tower goes to the catalytic cracker. The residual oil passes to the vacuum fractionating unit. Two fractions are removed and become feedstock for the catalytic cracker. The remaining heavy residue is called pitch and passes through a deasphalting unit which produces asphalt and some heavy oil. The asphalt is used in blending heavy fuel oils for industrial use. The remaining heavy oil is hydrotreated to remove sulfur and is fed to the catalytic cracker.

The fluid catalytic cracker (FCC) receives these heavy gas oils and residuals as feedstocks and yields four major fractions: clarified oil, heavy gas oil, naphtha and gasoline. The clarified oil and heavy gas oil are blended to yield heavy industrial fuel oil. The naphtha is chemically treated and serves as a gasoline blending component.

The gasoline from the catalytic cracker and most gases generated in the plant go to the gas recovery unit. The gasoline receives some initial treatment, is chemically treated further and becomes a part of the gasoline blending pool. The gases are recovered and separated for additional usage. Some become refinery fuel gas. Propane is stored and sold commercially. Isobutane goes directly to the alkylation unit. Normal butane, butylene, propane, propylene and some isobutane are treated for sulfur removal, then pass on to the alkylation unit. The alkylation unit puts these components together, yielding a high octane gasoline blending component. All of these various blending components are utilized to yield three grades of motor gasoline.

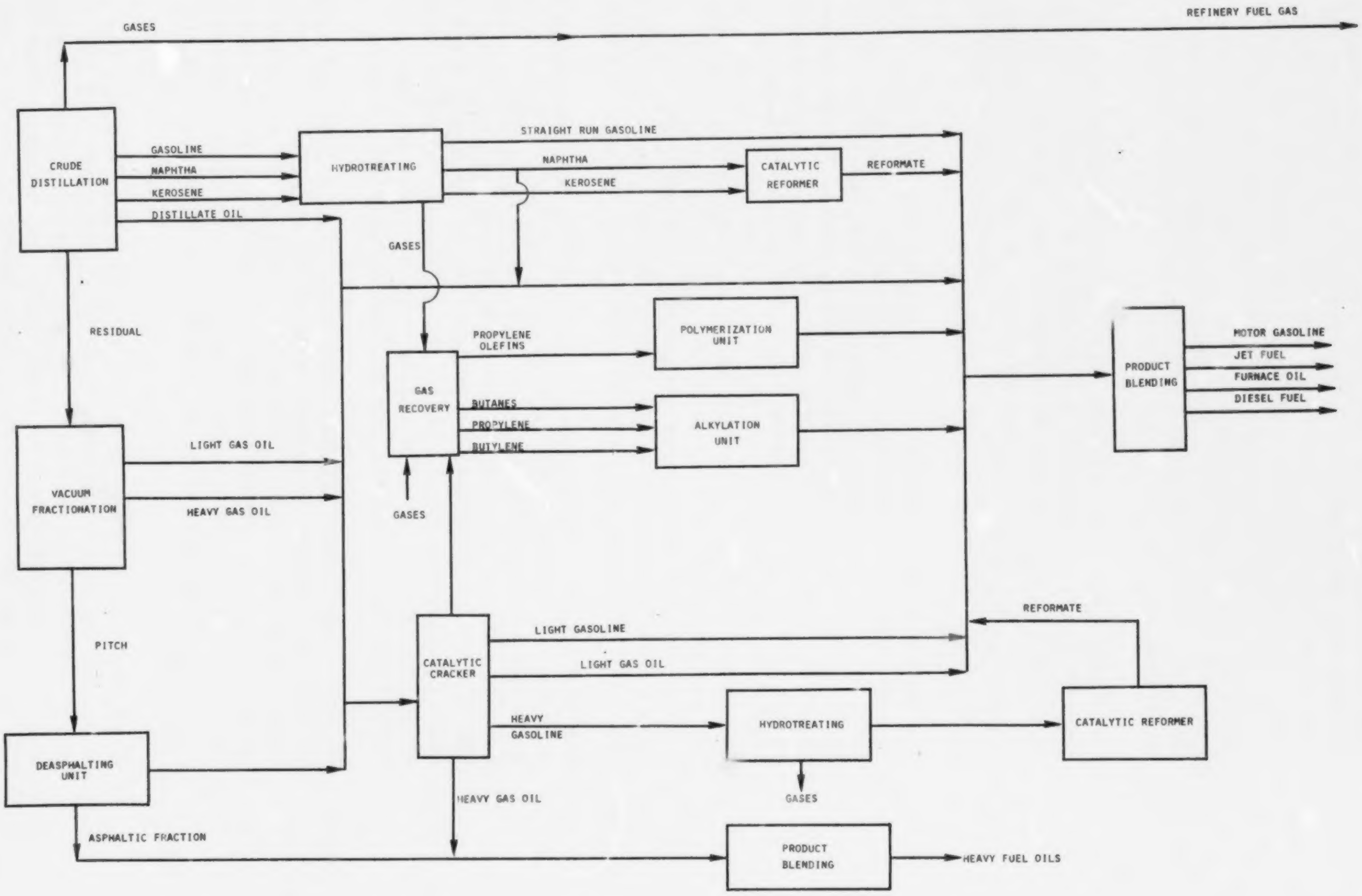
The refinery has two steam-stripping units for removing hydrogen sulfide and ammonia from sour process waters. This eliminates any hazard to personnel and reduces objectional odors. Additional benefits of the steam-strippers are the reduction of loading on the biological treatment processes, the release of excess heat and an adjustment of the pH of the oily-water stream. Waste acids and caustic solutions also receive some in-plant pretreatment prior to release to the wastewater treatment plant.

d. Texaco. The Texaco refinery was completed in 1958 and expanded in 1974 to provide additional processing capacity and octane improvement facilities. The major processes at the refinery are: crude desalting, atmospheric and vacuum distillation, butane deasphalting, hydrotreating, catalytic reforming, catalytic cracking, polymerization, alkylation and product finishing (see Figure 13).

Crude oil entering the refinery is processed first at the crude distillation unit composed of the crude desalter and the atmospheric distillation process. In the desalter, excess water and salts are removed from the crude oil. The crude is then heated and passed to the distillation tower where it is fractionated.

Figure 13

Refining Process Configuration at the Texaco Refinery


GASES
REFINERY FUEL GAS
CRUDE DISTILLATION
GASOLINE
NAPHTHA
KEROSENE
DISTILLATE OIL
HYDROTREATING
STRAIGHT RUN GASOLINE
NAPHTHA
KEROSENE
CATALYTIC REFORMER
REFORMATE
GASES
RESIDUAL
GAS RECOVERY
PROPYLENE OLEFINS
POLYMERIZATION UNIT
BUTANES
PROPYLENE
BUTYLENE
ALKYLATION UNIT
PRODUCT BLENDING
MOTOR GASOLINE
JET FUEL
FURNACE OIL
DIESEL FUEL
VACUUM FRACTIONATION
LIGHT GAS OIL
HEAVY GAS OIL
GASES
PITCH
CATALYTIC CRACKER
LIGHT GASOLINE
LIGHT GAS OIL
REFORMATE
HEAVY GASOLINE
HYDROTREATING
CATALYTIC REFORMER
DEASPHALTING UNIT
HEAVY GAS OIL
GASES
ASPHALTIC FRACTION
PRODUCT BLENDING
HEAVY FUEL OILS

Light gases are removed and used as refinery fuel. Straight run gasoline is withdrawn from the tower and used as a blending component for motor gasoline. Naphtha and kerosene are hydrotreated and a portion of each fraction serves as feedstock for the catalytic reformer. The remaining portions of each fraction are blended to make aviation fuels. The catalytic reformer receives low octane feedstocks and utilizes a platinum or platinum/rhenium catalyst to raise the octane rating. This high octane reformate is used as a blending stock for motor gasolines.

A small portion of the hydrotreated naphtha fraction is combined with the remaining distillate fraction to make burner oil. The remaining heavy residual fractions go either directly to the catalytic cracker or to the vacuum fractionation unit. The vacuum unit produces three fractions, including a heavy pitch residue. The two lighter fractions are passed on to the catalytic cracker. The pitch is extracted in a deasphalting unit utilizing butane as a solvent. The deasphalted oil passes on to the catalytic cracker, while the petroleum asphalt fraction is blended with other heavy fractions (from the catalytic cracker) to yield heavy industrial fuel oil and some refinery fuel oil.

The fluid catalytic cracker uses a catalyst composed predominantly of alumina and silica to further refine the heavy feedstock fractions and produce the desired naphtha and distillate fractions. The naphtha is used as a blending component for motor gasoline. The distillate fraction is used to produce diesel fuels. The heaviest fraction is blended with asphalt to produce heavy industrial fuel oils. The gases produced in the catalytic cracker join with all other gases produced in the refinery and pass to the gas recovery unit. This unit supplies the alkylation and polymerization units.

Propylene and other olefin feedstocks are "hooked together" in the polymerization unit to yield a higher octane blending component for gasoline. The alkylation unit utilizes iso- and normal butane, propylene and butylene to produce a high octane blending component for motor gasoline and jet fuel. Texaco has two alkylation units; however, only one is presently operating. The second unit was built to allow production of unleaded gasoline, but presently this additional product is not being produced.

The spent acid from the alkylation unit is reconstituted at the nearby Allied Chemical Company plant. Sour water from the crude desalter and catalytic cracker is steam stripped in the refinery to remove sulfides and ammonia. After stripping, the wastewater streams are fed to an oxidation unit for removal of remaining sulfides and thiosulfates. The gases obtained from these two in-plant processes are burned in a crude oil unit furnace. The stripped and oxidized condensates are discharged to the process wastewater sewer for final treatment in the wastewater treatment plant.

e. U.S. Oil & Refining. The refinery operated by U.S. Oil & Refining receives two very different types of crudes and keeps them separated throughout most of the process units. A heavy crude is used in the production of asphalt and a lighter crude is used for producing distillate fuels. The processes employed for treatment of heavy crude are atmospheric and vacuum distillation. The light crude passes through both atmospheric and vacuum distillation, and catalytic reforming (Figure 14).

The heavy crude is kept heated so that its viscosity is low enough to allow pumping. It passes into the atmospheric distillation tower and is separated into distillates and a heavy residual fraction. The heavy residue is used for making asphalt and goes to the asphalt tankage area for future blending. The distillate fractions are sold as diesel fuel oils.

The light crude also undergoes atmospheric and vacuum distillation, but in facilities separate from those used for the heavy crude. This yields four major fractions; gasoline, naphtha, kerosene and diesel fuel oil. A portion of these distillates, primarily low octane gasoline and naphtha from the vacuum unit, serves as feedstock for the catalytic reformer. The remainder of the distillates and the high octane reformate produced by the catalytic reformer are used as blending stocks for gasoline, jet fuel, and diesel fuel oil.

f. Sound Refining. Sound Refining operates a small 4,500 BPD capacity refinery in Tacoma, Washington. It is a simple refinery, producing predominantly petroleum asphalt (Figure 15). Heavy crude oil is pre-heated (it must be heated to move it) and injected into an atmospheric distillation tower, where fractionation occurs. Seven fractions are withdrawn from the tower. Gasoline and overhead gases are treated to remove water vapor, then join the withdrawn naphtha, kerosene, diesel and gas oil fractions in the distillate storage tanks, and are used to make heavy fuel oils and blending stocks for the production of special asphalt.

The heaviest fraction of the reduced crude is again heated and passes on to a vacuum distillation unit. The overhead vapors are treated for removal and condensation of water vapor. The treated gases go on to the distillate storage tanks along with two other fractions, the light and heavy lubricating oils. The remaining fraction from the vacuum unit is petroleum asphalt and is withdrawn to the asphalt storage tanks.

The new management of Sound Refining, which assumed control of the refinery on 1 July 1976, is not entirely satisfied with the

Figure 14

Refinery Process Configuration at the U.S. Oil & Refining Refinery

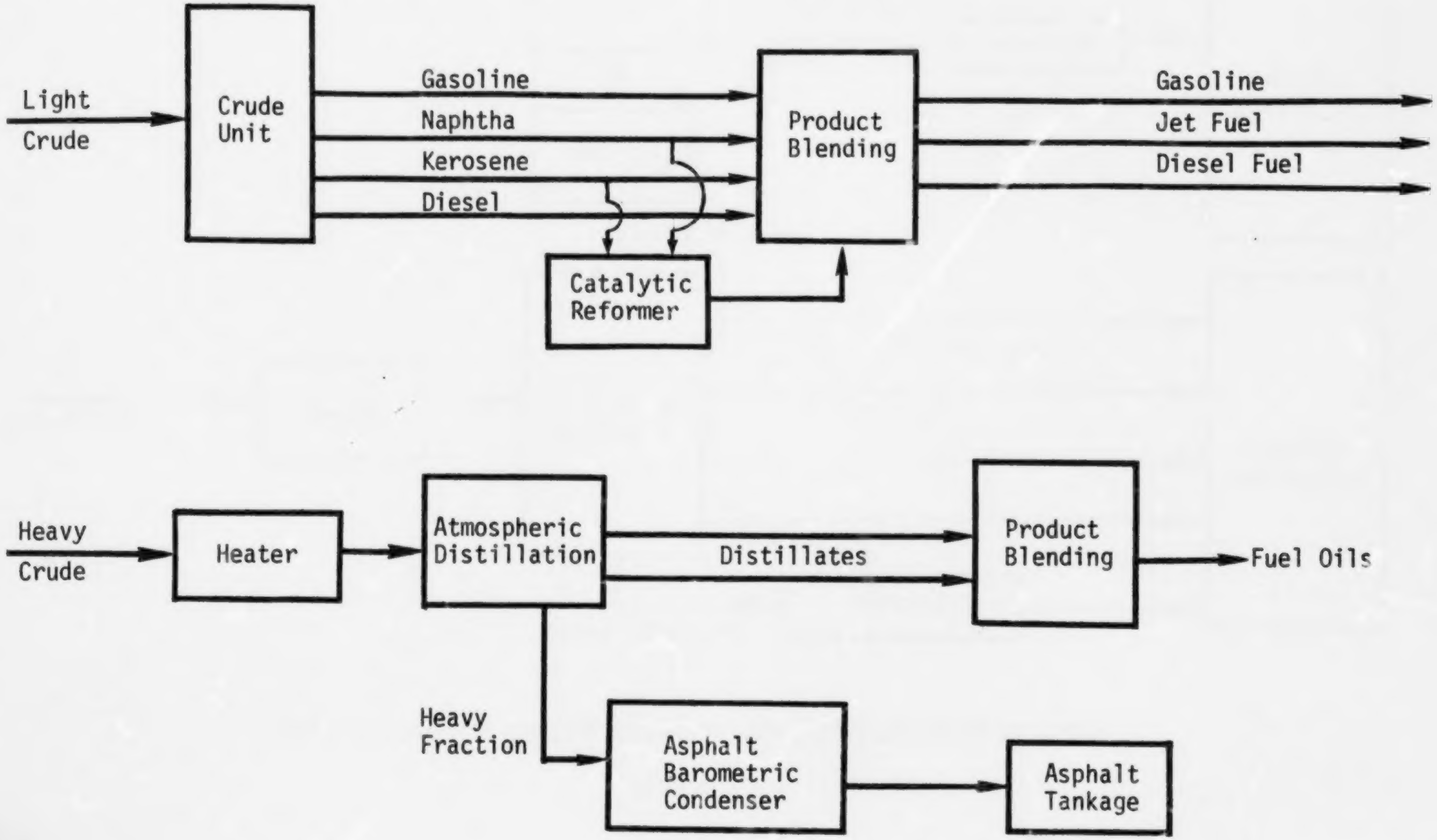
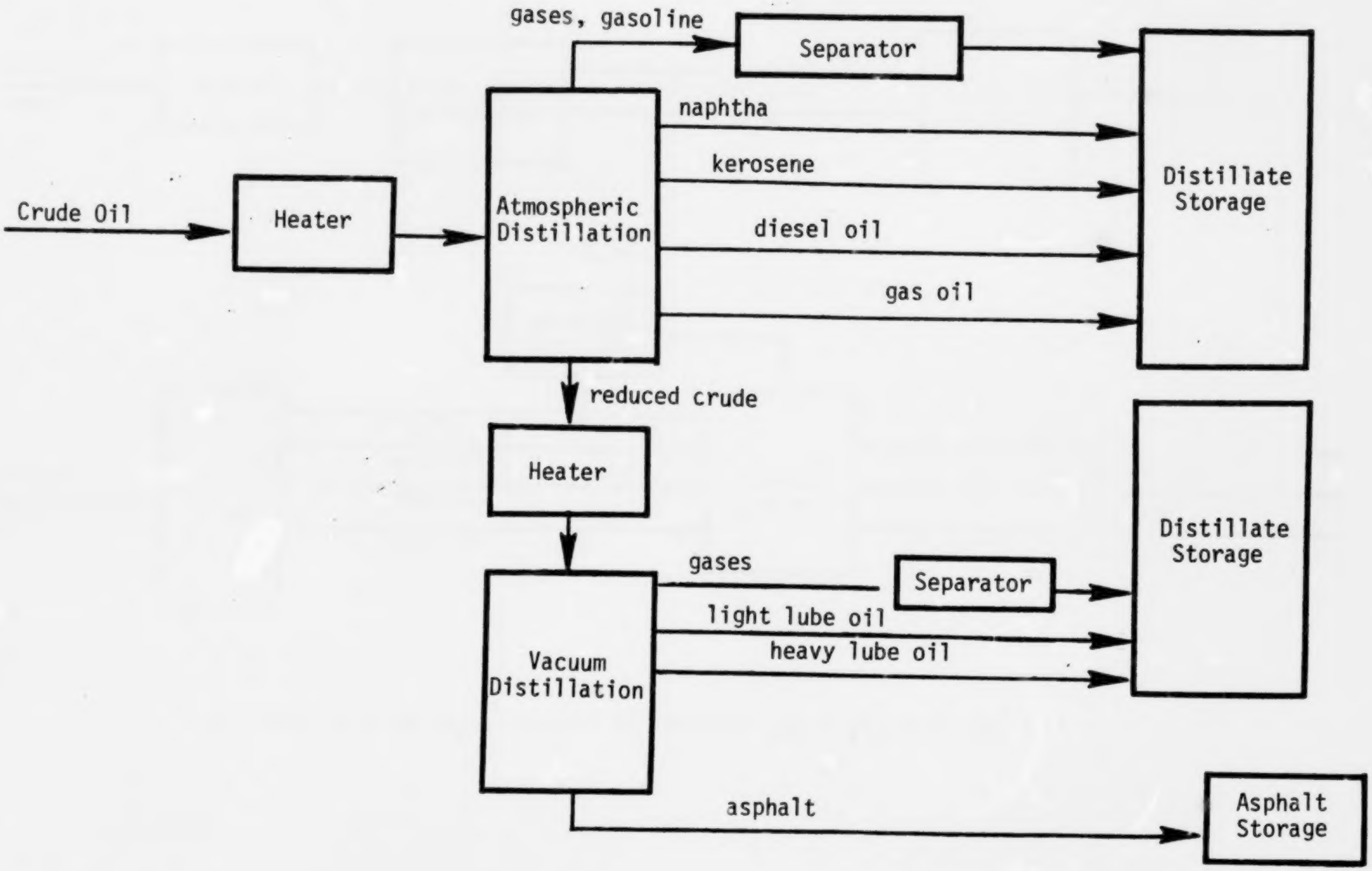

Light
Crude
Crude Unit
Gasoline
Naphtha
Kerosene
Diesel
Catalytic Reformer
Product Blending
Gasoline
Jet Fuel
Diesel Fuel
Heavy
Crude
Heater
Atmospheric Distillation
Distillates
Product Blending
Fuel Oils
Heavy Fraction
Asphalt Barometric Condenser
Asphalt Tankage

Figure 15

Refinery Process Configuration at the Sound Refining Refinery


gases, gasoline
Separator
naphtha
kerosene
Crude Oil
Heater
Atmospheric Distillation
Distillate Storage
diesel oil
gas oil
reduced crude
Heater
Distillate Storage
gases
Separator
light lube oil
heavy lube oil
Vacuum Distillation
asphalt
Asphalt Storage

present scheme of operations and is considering revising the refinery processes and utilizing different crude oils than have been used in the past.

E. Characteristics of Wastewater Entering the Treatment Plant

1. Introduction

Each process employed in a petroleum refinery yields a fairly characteristic wastewater. Observations from other refineries provide good indications of the types of contaminants to expect from the processes utilized in a given refinery. Knowledge of the overall types of pollutants to be found in the wastewater is essential for design of the waste treatment plant and the selection of treatment processes. In general, the parameters found in the influent to the wastewater treatment plant are: phenols, sulfides, BOD, COD, ammonia, oil, chlorides, alkalinity or acidity, suspended solids and a variable pH. Which of these pollutants are present and in what quantities depends on the processes in the refinery (see Table 46). Some general ranges of quantities of BOD, phenols and sulfide for petroleum refineries are shown in Table 47.

2. Characteristics of Wastewater from Refinery Processes

a. Crude Desalting. Wash water from the crude desalter units will contain ammonia, phenols, sulfides and suspended solids. All of these pollutants combine to produce a high BOD and COD. Some free oil is present, along with emulsified oil. The salts present, particularly chlorides, contribute to the high dissolved solids content of the process wastewater.

b. Crude Fractionation. The wastewater produced by atmospheric distillation and vacuum fractionation is generally a major source of ammonia and sulfides, especially when sour (high sulfur) crudes are being distilled. It also contains phenols, oil, mercaptans and chlorides.

c. Thermal Cracking. The major source of wastewater in thermal cracking is the overhead accumulator on the fractionator, where water is separated from hydrocarbon vapors, and is passed along to the sewer system. This wastewater usually contains ammonia, phenols, sulfides and oil. These cause high BOD and COD values. Alkalinity may also be high in wastewaters from thermal cracking units.

d. Catalytic Cracking. Catalytic cracking units are one of the largest sources of sour and phenolic wastewaters in a refinery. Wastewater comes from the steam strippers and overhead accumulators on the fractionators used to recover and separate the various hydrocarbon fractions produced in the reactor. The major pollutants are oil, phenols, sulfides, ammonia and cyanide.

Table 46

Qualitative Evaluation of Wastewater Characteristics by Refinery Process

Production Processes	Flow	BOD	COD	Phenol	Sulfide	Oil	Emulsified Oil	pH	Temp.	Ammonia	Chloride	Acidity	Alkalinity	Susp. Solids
Crude Oil and Product Storage	XX	X	XXX	X		XXX	XX	0	0	0		0		XX
Crude Desalting	XX	XX	XX	X	XXX	X	XXX	X	XXX	XX	XXX	0	X	XXX
Crude Distillation	XXX	X	X	XX	XXX	XX	XXX	X	XX	XXX	X	0	X	X
Thermal Cracking	X	X	X	X	X	X		XX	XX	X	X	0	XX	X
Catalytic Cracking	XXX	XX	XX	XXX	XXX	X	X	XXX	XX	XXX	X	0	XXX	X
Hydrocracking	X			XX	XX				XX	XX				
Polymerization	X	X	X	0	X	X	0	X	X	X	X	X	0	X
Alkylation	XX	X	X	0	XX	X	0	XX	X	X	XX	XX	0	XX
Isomerization	X													
Reforming	X	0	0	X	X	X	0	0	X	X	0	0	0	0
Solvent Refining	X		X	X	0		X	X	0			0	X	
Asphalt Blowing	XXX	XXX	XXX	X		XXX								
Dewaxing	X	XXX	XXX	X	0	X	0							
Hydrotreating	X	X	X		XX		0	XX		XX	0	0	X	0
Drying and Sweeteing	XXX	XXX	X	XX	0	0	X	XX	0	X	0	X	X	XX

XXX - Major Contribution, XX - Moderate Contribution, X - Minor Contribution, 0 - No Problem, — No Data

Source: (32)

Table 47

Average Wastewater Loadings from Petroleum Refineries Utilizing
Old, Prevalent, and New Technology

	Flow, gal/bbl		BOD, lb/bbl		Phenol, lb/bbl		Sulfide, lb/bbl	
Type of Technology	Avg	Range	Avg	Range	Avg	Range	Avg	Range
Older	250	170–374	0.40	0.31–0.45	0.030	0.028–0.033	0.01	0.008
Typical	100	80–155	0.10	0.08–0.16	0.01	0.009–0.013	0.003	0.0028
Newer	50	20–60	0.05	0.02–0.06	0.005	0.001–0.006	0.003	0.0015
	liters/bbl		g/bbl		g/bbl		g/bbl	
	945	644–1410	181	141–204	13.6	12.7–15	4.5	
	378	301–586	45.4	37.3–72.5	4.5	4.1–5.9	1.4	
	189	76–227	22.7	9.1–27.2	2.3	0.45–2.7	1.4	

Source: (15)

Reprinted with permission from:
Eckenfelder, W. W. Jr., Water Quality Engineering for Practicing Engineers.
Barnes & Noble. 1970.

The phenol and sulfide concentration will vary with the type of crude being processed. All of these contaminants contribute to a wastewater with high alkalinity, BOD and COD.

e. Hydrocracking. Wastewater from this unit contains sulfides, phenols, and ammonia, since one purpose of hydrocracking is to yield a clean product relatively free of sulfur and nitrogen. Most of these compounds are in the gas products which are sent to a treating unit for removal and recovery of sulfur and nitrogen. However, some of these contaminants will be found in the process wastewater stream.

f. Polymerization. Even though this process utilizes acid catalysts, the wastewater stream is alkaline because most of the catalyst is recycled and any remaining acid is removed by caustic washing. Most of the contaminants arise from the pretreatment of the feedstock. The wastewater is high in mercaptans, sulfides and ammonia.

g. Alkylation. The major discharge from this process is the spent caustic from the neutralization of the hydrocarbon stream leaving the reactor. These wastewaters contain dissolved and suspended solids, oils, sulfides, chlorides and ammonia. Water drawn off from the overhead accumulators contribute to BOD, COD, oil and sulfide levels, but is not a major source of wastewater from this process.

h. Isomerization. This is a fairly clean process and the wastewater from this unit contains no major pollutants, only minor contributions of phenols and BOD.

i. Reforming. Reforming is also a relatively clean process. Very little water is used in the process and none of the wastewater streams have a significant amount of contaminants. The wastewater is generally alkaline and contains some sulfides, ammonia, oils and mercaptans from the overhead accumulator of the stripping tower.

j. Hydrotreating. The quantity of wastewater generated by hydrotreating, hydrorefining and hydrofinishing depends on which process is used and the type of crude employed as a feedstock. Ammonia and sulfides are the major pollutants, but phenols may also be a problem.

k. Product Finishing. Generally much care is taken to prevent any loss of product, so the blending of products produces no major contaminants. The main source of wastewater results from the washing of tanks and railroad tank cars prior to storage or loading of finished products. These wash waters are particularly high in emulsified oils.

3. Influent Wastewater Characteristics for the Washington Refineries

On the whole, no consistent monitoring of the wastewater entering the treatment plant is made at any of the six refineries. The refineries are more concerned with measuring pollutants in the final effluent from the wastewater treatment plant. Furthermore, in many cases it would be difficult to make any meaningful assessment of influent characteristics because the wastewater streams are separated into different collection systems. Each separate stream would have to be analyzed for the quantity of each pollutant. The sum of these assessments could tentatively be used to represent the quality of the refinery wastewater. However, this would involve numerous difficulties and procedures which are of no impact on the actual running of the refinery. Possibly measurement of the influent wastewater would be more appropriate after the first treatment process of the main wastewater stream. Such measurements have been made at the Shell refinery on occasion, using the effluent from the API separator. A typical analysis is shown below. No breakdown of oil and grease into hydrocarbon types is available.

Influent Characteristics - API Separator Outfall

	Concentration (mg/l)		
Parameter	Maximum	Minimum	Mean
Total Suspended Solids (TSS)	216	19	68
Ammonia (as Nitrogen)	161	98	123
Sulfide	37	11	23
Chemical Oxygen Demand (COD)	583	190	281
Biological Oxygen Demand (BOD)	228	70	118
Phenols	12	1	10
Hexavalent Chromium	-	-	-
Total Chromium	2.6	0.8	0.88
Oil and Grease	60	11	31
Fecal Coliform	-	-	-
pH	11.5	10.3	10.9

This also may be indicative of the levels of pollutants entering the wastewater treatment plants at Texaco and Mobil which employ similar crude oils and refinery processes. However, no definite statement can be made regarding the pollutants entering the wastewater treatment plants beyond a general qualitative assessment based on the refinery processes being utilized.

F. Ballast and Stormwater Flows

1. Introduction

Ballast and stormwater flows are difficult to assess in a refinery for two reasons. First of all, in the major refineries, the wastewater streams are separated into separate sewer systems. Secondly, flow measurements of these parameters are of relatively little concern for those operating a refinery. So, little consideration is given to ballast and stormwater volumes; instead the total effluent discharge is monitored.

2. Ballast Water

Ballast water is received at the refinery from ships which are loading refined products. This water is kept in storage tanks prior to its release to the wastewater treatment plant. Often ballast water is released to the treatment system primarily to equalize wastewater flows and smooth out low flow periods. In some instances the water may be skimmed for oil removal while in the ballast water storage tank. However, treatment of the water is usually accomplished within the wastewater treatment plant itself (described in Section II-G).

Neither U.S. Oil & Refining or Sound Refining receive ballast water from incoming or outgoing ships. The remaining four refineries are allocated certain average and maximum volumes of ballast water in their National Pollutant Discharge Elimination System (NPDES) discharge allocations regarding total effluent discharge. The ballast water flow allocations are based on either the actual discharge from the ship or the flow from the ballast water storage tank. The average ballast water flow allocation is based on an assumed processing of one ship's ballast discharge every ten days. The maximum flow allocation is based on the actual daily rate of flow from the ballast water storage tank. These allocations are shown in Table 48. Actual ballast water flows for 1974, 1975 and the first half of 1976 from the Shell refinery are shown in Table 49. The averages are offloading values and the maximum values are the volume of ballast water discharged from the ballast water storage tank.

Besides providing a ballast water flow allocation, the NPDES permit allows an additional pollutant loading in the final effluent, based on the ballast water discharge. Allocation factors have been established for each individual refinery by the Department of Ecology for specific parameters; oil and grease, BOD, COD and suspended solids. These allocation factors (in lbs/gal) are multiplied by the ballast water flow allocation to yield the additional allowable quantities of pollutants in the refinery's final effluent discharge.

3. Stormwater

Stormwater is the precipitation that falls on the refinery grounds. In the four major refineries this water may enter two different sewer systems, depending on where in the plant it fell. Stormwater that is from non-oily, non-process areas is collected in a clean water sewer system at Mobil, ARCO, Texaco and Shell. This relatively uncontaminated water receives a minimum of treatment in the wastewater treatment plant, although it is always possible to shunt the stormwater into the main process stream to receive more extensive treatment if contamination occurs. Stormwater that falls on oily, process areas is collected along with other contaminated wastewater and receives a full range of physical and biological treatment. There are usually large holding basins to contain

Table 48

Average and Maximum Ballast Water Flow Allocations (in Thousands Gallons Per Day)

	Mobil	ARCO	Shell	Texaco
Average	185	330	60	NA§
Maximum	550	800	NA	NA

§Not Available

Table 49

Ballast Water Flows for 1974-1976 from the Shell Refinery (in Thousands Gallons Per Day)

	1974	1975	1976 (Six Months)
Average	30.4	40.4	57.1
Maximum	618	872	907

Source: (19)

the stormwater flows and to prevent surges in the wastewater flow. The water is released for treatment according to the flow levels in the treatment plant. U.S. Oil & Refining and Sound Refining do not have separate sewer systems; all wastewater, including stormwater, receives the same treatment.

Like ballast water, the NPDES discharge permits allocate certain average and maximum volumes of stormwater. The stormwater flow allocations are based on an average precipitation figure or a single day peak rainfall. The average stormwater allocation is based on an annual average of 35 inches of precipitation per year. The maximum stormwater flow is based on a peak rainfall of 2.5 inches per twenty-four hour period. These rainfall values are multiplied by the storm sewer collection area to yield the average and maximum allocations. These allocations will vary from refinery to refinery because of differences in land area. The stormwater flow allocations for the Puget Sound refineries are shown in Table 50. These values assume total runoff of rainfall; with no losses to ground water or evaporation. It is often difficult to accurately distinguish and account for the actual volumes of stormwater received. This is especially true when stormwater goes to separate systems and is mixed in with other types of wastewater. However, some measurements are possible, and the stormwater flows for 1974-1976 from the Shell refinery are shown in Table 51.

Besides providing a flow allocation, the NPDES discharge permit allows an additional pollutant loading, based on the stormwater discharge. As with ballast water, allocation factors have been established for each refinery for specific parameters: oil and grease, BOD, COD, and suspended solids. These allocation factors (in lbs/gal) are multiplied by the stormwater flow allocation to yield the additional allowable quantities of pollutants in the refinery's final effluent discharge.

G. Wastewater Treatment Processes

1. Introduction

In general, the types of wastewater produced in a refinery depend on the crudes and processes utilized. Each refinery process yields wastewater which has fairly specific chemical contaminants and characteristics. It is these parameters and the required degree of treatment to fulfill effluent standards which are considered in the design and operation of a refinery wastewater treatment plant. The major types of waste treatment processes available for consideration are: API separators, oxidation ponds, air flotation, clarification, coagulation and flocculation, aeration basins, activated sludge, trickling filter, rotating biological surface units, polisher units and activated carbon. Typical removal efficiencies of these processes and the expected effluent from each process are shown in Tables 52 and 53.

Table 50

Average and Maximum Stormwater Flow Allocations (in Million Gallons Per Day)

	Mobil	ARCO	Shell	Texaco	U.S. Oil & Refining	Sound Refining
Average	0.31	0.55	0.72	NA[§]	NA	0.03
Maximum	7.1	8.0	18.8	NA	NA	NA

[§] Not available

Table 51

Stormwater Flows for 1974, 1975 and the First Half of 1976 from the Shell Refinery (in Million Gallons Per Day)

	1974	1975	1976 (Six Months)
Average	0.41	0.62	0.53
Maximum	11.0	10.1	6.3

Source: (19)

Table 52

Typical Removal Efficiencies for Oil Refinery Treatment Processes

PROCESS	PROCESS INFLUENT	REMOVAL EFFICIENCY, % BOD_5	COD	TOC	SS	OIL	PHENOL	AMMONIA	SULFIDE
1. API Separator	Raw Waste	5-40	5-30	NA	10-50	60-99	0-50	NA	NA
2. Clarifier	1	30-60	20-50	NA	50-80	60-95	0-50	NA	NA
3. Dissolved Air Flotation	1	20-70	10-60	NA	50-85	70-85	10-75	NA	NA
4. Filter	1	40-70	20-55	NA	75-95	65-90	5-20	NA	NA
5. Oxidation Pond	1	40-95	30-65	60	20-70	50-90	60-99	0-15	70-100
6. Aerated Lagoon	2,3,4	75-95	60-85	NA	40-65	70-90	90-99	10-45	95-100
7. Activated Sludge	2,3,4	80-99	50-95	40-90	60-85	80-99	95-99+	33-99	97-100
8. Trickling Filter	1	60-85	30-70	NA	60-85	50-80	70-98	15-90	70-100
9. Cooling Tower	2,3,4	50-90	40-90	10-70	50-85	60-75	75-99+	60-95	NA
10. Activated Carbon	2,3,4	70-95	70-90	50-80	60-90	75-95	90-100	7-33	NA
11. Filter Granular Media	5-9	NA	NA	50-65	75-95	65-95	5-20	NA	NA
12. Activated Carbon	5-9 plus 11	91-98	86-94	50-80	60-90	70-95	90-99	33-87	NA

NA - Data Not Available

Source: (32)

Table 53

Expected Effluents from Petroleum Treatment Processes

PROCESS	PROCESS INFLUENT	EFFLUENT CONCENTRATION, mg/L							
		BOD_5	COD	TOC	SS	OIL	PHENOL	AMMONIA	SULFIDE
1. API Separator	Raw Waste	250-350	260-700	NA	50-200	20-100	6-100	15-150	NA
2. Clarifier	1	45-200	130-450	NA	25-60	5-35	10-40	NA	NA
3. Dissolved Air Flotation	1	45-200	130-450	NA	25-60	5-20	10-40	NA	NA
4. Granular Media Filter	1	40-170	100-400	NA	.5-25	6-20	3-35	NA	NA
5. Oxidation Pond	1	10-60	50-300	NA	20-100	1.6-50	0.01-12	3-50	0-20
6. Aerated Lagoon	2,3,4	10-50	50-200	NA	10-80	5-20	0.1-25	4-25	0-0.2
7. Activated Sludge	2,3,4	5-50	30-200	20-80	5-50	1-15	0.01-2.0	1-100	0-0.2
8. Trickling Filter	1	25-50	80-350	NA	20-70	10-80	0.5-10	25-100	0.5-2
9. Cooling Tower	2,3,4	25-50	47-350	70-150	4.5-100	20-75	.1-2.0	1-30	NA
10. Activated Carbon	2,3,4	5-100	30-200	NA	10-20	2-20	<1	10-140	NA
11. Granular Media Filter	5-9	NA	NA	25-61	3-20	3-17	0.35-10	NA	NA
12. Activated Carbon	5-9 and 11	3-10	30-100	1-17	1-15	0.8-2.5	0-0.1	1-100	0-0.2

NA - Data not available

Source: (32)

2. General Wastewater Treatment Process Description

a. Gravity Separation. The API separator is the most common type of gravity separator and is used as primary treatment for the removal of oil and grease. Most or all of the water from the separate refinery sewer systems passes through an API separator in a refinery. For some types of effluent, such as uncontaminated stormwater, this process may be the sole treatment which the wastewater undergoes. Available performance data indicates a range of 60-99 percent removal of the oil content of influent water. Some removal of phenols, BOD and COD is also accomplished, along with suspended solids which settle to the bottom of the separator.

The basic design of an API separator is a long rectangular basin with a long enough retention time of the wastewater to allow the oil to float to the surface and be removed. Most separators are divided into more than one bay, to make the process more effective. Scrapers are provided to move the oil downstream to a slotted pipe or a drum where the oil is collected. On their return upstream, the scrapers travel along the bottom and move settled solids to a collection trough.

A modification of this basic design is the parallel plate separator. The separator chamber is subdivided by parallel plates set at 45° angle with horizontal and less than 6 inches apart. This increases the overall surface area of the unit and decreases the separation depth, thus allowing a decrease in size of the unit. Some separators use corrugated plates to increase the area even more. As water flows through the separator, oil droplets coalesce on the underside of the plates and travel upward to where the oil is collected.

b. Clarification. Clarifiers are often used in both primary and secondary treatment. Clarifiers use gravitational separation to remove oil and suspended solids from the wastewater stream. Surface skimmers are usually provided for more efficient removal of oil. Phenols, BOD, COD, suspended solids, ammonia, sulfides and oil are all removed by this process. Often chemical coagulants are employed to enhance flocculation and sedimentation of suspended materials. This may raise the removal efficiency of simple clarification as shown in Table 53.

c. Oxidation Ponds. Oxidation ponds are often used as a major treatment process, providing secondary treatment of wastewater after gravity separation. Some refineries use ponds as a final polishing process after all other treatment processes. The ponds are shallow and unaerated, but remain aerobic. The bacteria and algae present serve to reduce BOD, COD, suspended solids and inorganic nutrient levels. Ponds are usually sealed with clay, asphalt or polyethylene to prevent seepage. The retention time, depth and surface area are all factors which affect the removal efficiency of this process.

d. Air Flotation. The primary purpose of this process is the clarification of wastewater by the removal of suspended matter, including oil and grease. Air bubbles under pressure in the basin allow suspended material to adhere to the bubbles. The material rises to the surface where it is removed by skimming. This process also reduces BOD and COD by the removal of the suspended matter. The addition of air acts to lower the oxygen demand of the wastewater. Chemical flocculating agents may also be added to improve the effectiveness of air flotation and to obtain a higher degree of clarification. Mechanical equipment is necessary in the basin for continuous removal of the upper froth and the bottom sludge. Comparisons of the performances of clarifiers using chemical coagulation and the air flotation process indicate that flotation performs somewhat better.

e. Aeration Basins. Aeration basins are essentially upgraded oxidation basins. The use of surface aerators permits deeper ponds, shorter retention periods and less surface area. The retention times are reduced from the 20-110 days for oxidation ponds to 1-12 days when mechanical aerators are employed, and the removal efficiencies are usually higher.

f. Biological Treatment. Processes involving the use of bacteria or other microbes for the oxidation of wastes are called biological treatment. The overall biochemical reaction can be considered as occurring in two phases: (1) the synthesis of new microbial sludge or protoplasm, and (2) the auto-oxidation of part of the microbial sludge, which is referred to as endogenous metabolism. In the synthesis phase, nutrients in the wastewater are utilized in producing new microbial cells. In the endogenous metabolism phase, nutrients are released and either reused or oxidized.

i. Activated Sludge. There are many types of activated sludge processes. Although they vary in detail, the basic method is fairly uniform among various modifications. The wastewater is mixed with previously synthesized microbial organisms in a system supplied with air or mechanically aerated. Much of the colloidal and suspended material in the influent is adsorbed by the microbial sludge, greatly reducing BOD, COD, suspended solids, oil, phenols, sulfides and ammonia. Usually the aeration basin, where wastewater is contacted with microorganisms, is followed by a clarification basin. Here, the water is withdrawn while sludge containing microorganisms and contaminants settles to the bottom. A portion of the sludge is recycled to the aeration basin, while the remainder is collected and discarded.

ii. Trickling Filter. A trickling (trickle) filter consists of a fixed bed of rocks, slag or plastic media which has a thin layer of microbial slime covering it. The wastewater flows over the media and contacts the microbes for biological treatment. Aerobic conditions are maintained by air flowing through the bed. As the water trickles through the media, contaminants are removed by the microorganism population. For more efficient removal, the wastewater is recycled over the media bed. This process has good removal efficiencies for BOD, COD, sulfides, ammonia, phenols, oil and suspended solids, but as indicated in Table 53, activated sludge produces better results if properly maintained.

iii. Rotating Biological Surface Units (RBS). These units consist of horizontal cylindrical tanks which are filled with wastewater. A series of corrugated disks rotate about a central axis in the tank. Bacteria and other microbes are allowed to grow on the disks and provide biological treatment as they are rotated through the wastewater. The rotation of the disks exposes the microorganisms both to air and the wastewater, thus constantly renewing the bacteria-nutrient-oxygen interface. General removal efficiencies are not available for these units; however, they are highly rated for removal of phenols and they reduce BOD, COD, oil and sulfides. A polisher unit consisting of a media filter and a coalescer filter is usually linked with a rotating biological surface unit. Its purpose is to remove the material degraded in the RBS unit and provide a final clarification of the treated wastewater. Neither of these units is commonly employed by large refineries, due to flow limitations, size of the unit and the availability of other more efficient treatment processes. Usually they are limited to refineries of less than 30,000 BPD capacity.

g. Activated Carbon. The activated carbon process utilizes granular activated carbon to adsorb pollutants from the wastewater. The water flows through banks of carbon columns arranged in series or parallel. As the water moves past the columns, pollutants are adsorbed by the activated carbon, gradually filling the pores. At intervals portions of the carbon are removed to a furnace where the adsorbed substances are burned off, and the carbon is reused. Activated carbon reduces BOD, COD, oil, phenols, suspended solids, ammonia and sulfides, but is not yet widely utilized by the refining industry.

3. Wastewater Treatment Configurations For Puget Sound Refineries

a. Mobil. The wastewater treatment plant at Mobil's Ferndale refinery receives untreated water from five separate sewer systems and one drainage system. Many additions have been made since the initial plant construction in 1954, in a continuing effort to meet Federal and state regulations and minimize the effluent effects on the receiving waters. The most recent addition was in 1973, further upgrading the plant capacity and treatment abilities. The six different inputs of wastewater are kept separate to allow the adequate and appropriate treatment of each particular type of wastewater. Thus, all wastewater produced in the refinery and its operations are collected in one of the following systems: (1) storm, (2) ballast, (3) phenolic, (4) oily, (5) sanitary and (6) tank farm spillage. (See Figure 16).

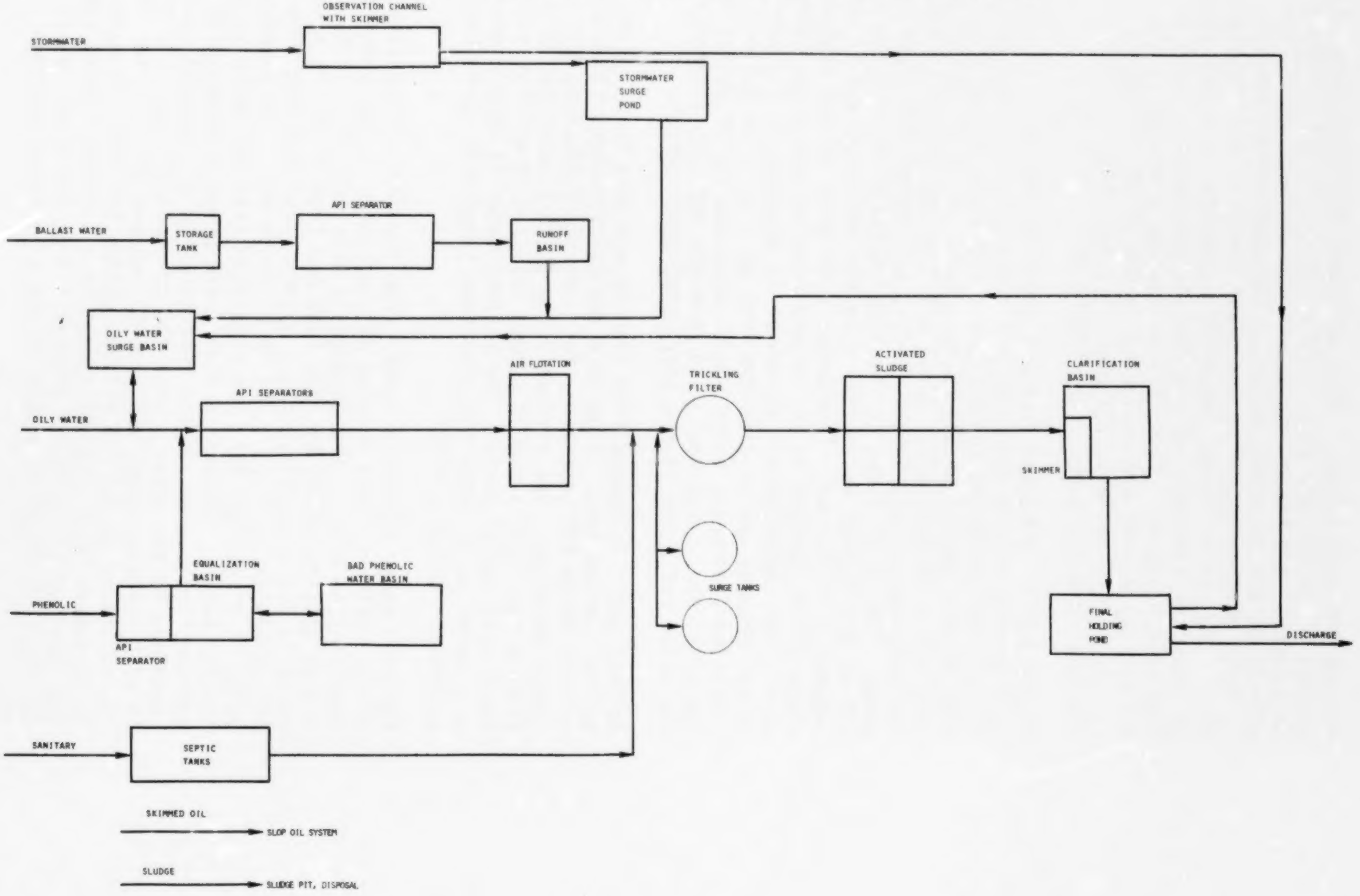
Stormwater is collected from all areas of the refinery. Treatment depends on the degree of oil contamination. Stormwater from non-contaminated run-off areas flows through an observation channel where any oil present tends to float to the surface and is skimmed off. Since oil from the ground surface is the only contaminant in this water, no further treatment is given. The water flows to the final holding pond, which receives all of the treated wastewater from the refinery, and is subsequently discharged. Stormwater from areas of the refinery where oil is present on the ground receives additional treatment. The contaminated stormwater is detected in the observational channel and is diverted into an 11 million gallon contaminated stormwater surge pond. Subsequently it passes into the oily water surge basin and receives the same treatment as the water collected in the oily water sewer system.

Ballast water is pumped from tankers and held in a 1.3 million gallon storage tank. From here the ballast water flows by gravity to an API separator, for removal of floating oil and oily sludge material. The effluent from the API separator passes through hay filters and is pumped into a 0.35 million gallon beach head runoff basin. The ballast water is then pumped to the oily water surge basin and processed along with contaminated stormwater and oily water.

Phenolic water and storm runoff from the product treating area of the refinery flows into an API separator in the phenolic equalization basin. Oil skimmed in this separator is stored in a 0.01 million gallon storage tank and transferred on a batch basis to the slop oil recovery system. The sediment from the API separator is disposed of in a sludge pit. The phenolic water is discharged from the separator into the phenolic equalization basin. Subsurface mixers are present to minimize the extreme fluctuations in the concentration of chemical contaminants contained in the water. When the contaminants are in a relatively high concentration, the phenolic waters are diverted from the separator to the 0.6 million gallon bad phenolic water basin. It is pumped back into the system at a limited rate to reduce the level of contaminants present. From the equalization basin, the phenolic water is pumped to the oily water treatment facilities.

Figure 16

Wastewater Treatment Configuration at the Mobil Refinery


OBSERVATION CHANNEL WITH SKIMMER
STORMWATER
STORMWATER SURGE POND
API SEPARATOR
BALLAST WATER
STORAGE TANK
RUNOFF BASIN
OILY WATER SURGE BASIN
API SEPARATORS
OILY WATER
AIR FLOTATION
TRICKLING FILTER
ACTIVATED SLUDGE
CLARIFICATION BASIN
SKIMMER
EQUALIZATION BASIN
BAD PHENOLIC WATER BASIN
SURGE TANKS
PHENOLIC
API SEPARATOR
FINAL HOLDING POND
DISCHARGE
SANITARY
SEPTIC TANKS
SKIMMED OIL
SLOP OIL SYSTEM
SLUDGE
SLUDGE PIT, DISPOSAL

Blowdown from treatment processes, which treat the raw water taken from the Nooksack River for various functions in the refinery, is collected in a 0.7 million gallon blowdown pit for clarification. From there the water is pumped to the oily water sewer.

Thus, after varying degrees of separate treatment, contaminated stormwater, ballast water, phenolic water and raw water treatment blowdown water all eventually empty into the oily water sewer for further treatment. These waters combine with oily water and stormwater runoff from the process areas and pass through a pH control sump. Sulfuric acid or spent caustic is added to the water to control the pH of the water for optimum biological treatment. Phosphoric acid is also added at this point to provide a necessary nutrient for the biological system.

The combined water next flows into two large API separators. These separators are in parallel so that one can be shut down for maintenance and repair, without affecting the treatment facility. Any excessive flow which cannot be handled by the remaining separator can be temporarily held in the oily surge basin, to be treated later. Skimmed oil from these separators is pumped to the slop oil system and the bottom solids are diverted to the sludge pit for storage until final disposal. The water effluent from the API separators passes on to two parallel air flotation tanks for additional oil recovery. The oily froth from these units is recycled to the slop oil recovery unit.

The wastewater is joined here by sanitary wastes from the various septic tanks at the refinery and is pumped to the trickling filter. If the flow volume is too great, some of the water can be diverted to two 0.42 million gallon surge tanks. A pumping station is present to recycle water for the trickling filter and to move the water to the next state of biological treatment. Four parallel activated sludge units provide additional biological treatment of the combined wastewater flow. Two of the units are equipped with a recycle stream for additional aeration and to provide a constant source of microorganisms for the activated sludge units in case of any loss of the bacteriological population.

The final effluent from the activated sludge tanks is pumped to a 5.0 million gallon clarification pond for sedimentation of biological-flocculent carry-over. A skimmer is present in the pond to remove any floating oil or other material. This water is then pumped to the 10.0 million gallon final holding pond prior to discharge into Puget Sound. The clarification pond can be bypassed during periods of maintenance and repair with the effluent from the activated sludge units being pumped directly to the final holding pond. In case the effluent quality does not meet the allowable levels of contaminants, the flow is diverted to the oily surge basin for retreatment. The uncontaminated storm runoff also enters the final holding pond and is mixed with the treated wastewater. The total plant effluent is then pumped through the outfall line and diffuser into the Strait of Georgia.

b. ARCO. Atlantic Richfield's wastewater treatment plant at Cherry Point was specifically designed to comply with the strict Washington State Standards for water quality. Extensive effort was made to employ the best process available to treat the newly constructed refinery's wastewater. The facility was designed for twice the expected dry weather flow, to provide surge capacity to handle peak flows and to allow shutdown of equipment for maintenance and cleaning without affecting the treatment plant operation. Four separate systems handle all of the wastewater occurring at the plant. Each system involves wastewater from different sources, requiring different types and degrees of treatment, but are set up in such a manner that wastewater volumes may be shunted to other systems for additional treatment. The four collection and treatment systems are for the following types of wastewater: clean, ballast, process and sanitary (see Figure 17).

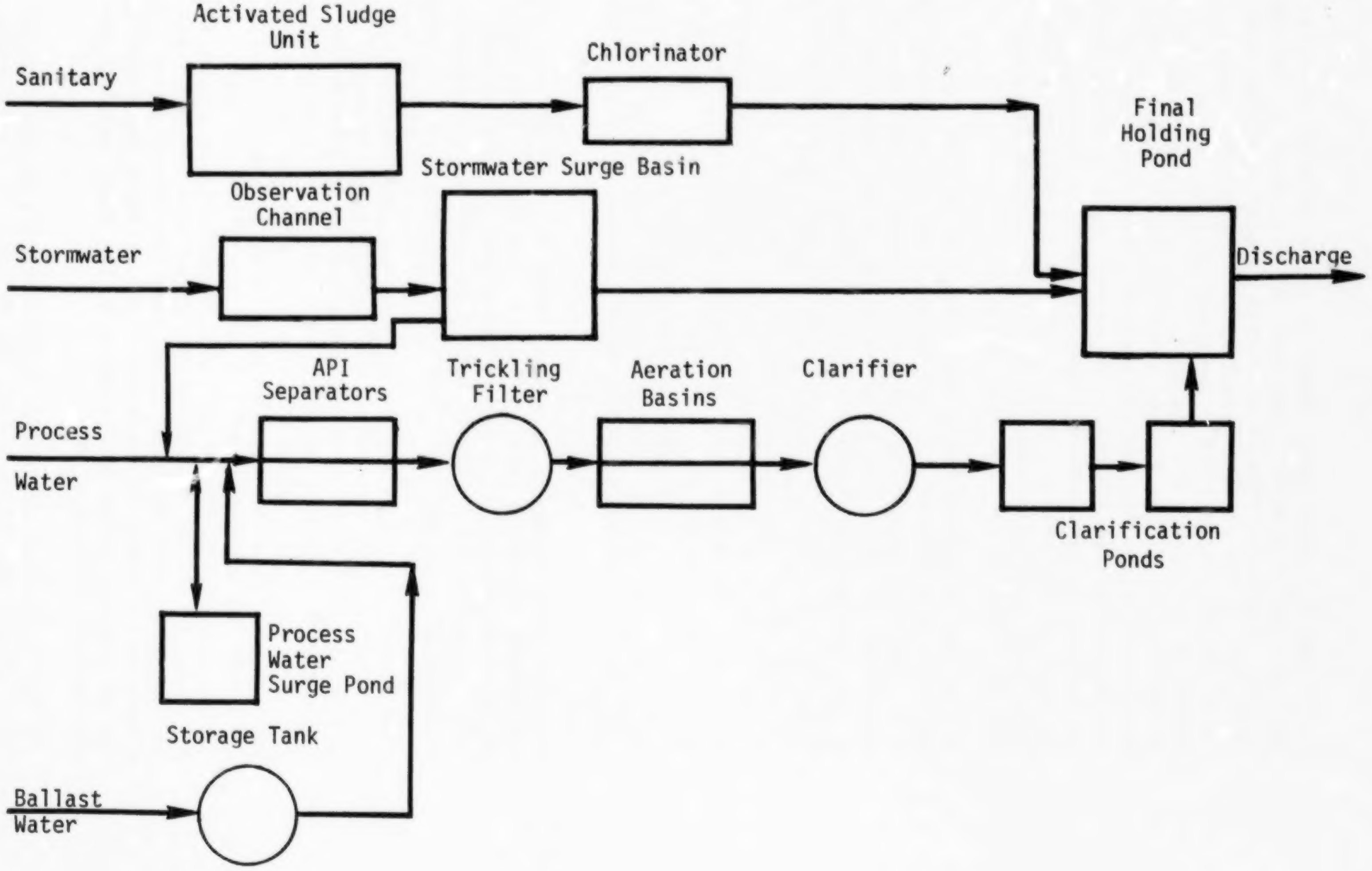
The clean water system includes clean water from the refinery processes and stormwater from uncontaminated areas of the refinery. The sewer system which collects the stormwater from all non-process areas and receives water from the boiler and cooling tower blowdown streams is equipped with a trash rack to remove debris and a floating oil skimmer to remove any oil present in the waters. The effluent from this channel is monitored for total organic carbon content and oil and grease concentrations and is discharged to the 7.5 million gallon stormwater surge pond. If the water is considered clean enough, it is discharged to the 7.5 million gallon final holding pond or directly to the outfall diffuser at the refinery dock. If the water is determined to need further treatment, it is shunted from the observation channel or the stormwater surge pond to the process water treatment system prior to the initial treatment stage (the API separators).

Ballast water from arriving product ships is pumped to a 4.2 million gallon tank equipped with a floating oil skimmer. The oil recovered is de-watered and reused in the refinery processes. The ballast water in the tank is monitored and if it is uncontaminated it may be routed directly to the final holding pond and/or to the outfall diffuser. Normally, though, the ballast water is passed over to the process water treatment system, prior to the API separators.

The process or oily water system collects all wastewater which may be contaminated from the refinery processes or other sources. All water from the vehicle garage drains, process area washdown, sample flush drains, laboratory sinks, stormwater from oily process areas, product wash water, stripped process sour water,

Figure 17

Wastewater Treatment Configuration at the ARCO Refinery


Activated Sludge Unit
Chlorinator
Sanitary
Final Holding Pond
Stormwater Surge Basin
Observation Channel
Stormwater
Discharge
API Separators
Trickling Filter
Aeration Basins
Clarifier
Process Water
Clarification Ponds
Process Water Surge Pond
Storage Tank
Ballast Water

spent caustic, spent water from the crude desalter and contaminated ballast water flows into the oily water collection system. The spent caustic will have already undergone pretreatment in the chemical treating unit, where most acidic materials are neutralized. The crude desalter water, contaminated with crude oil and salt, contributes a large portion to the loading of the process water treatment system. This may be reduced by reusing stripped sour water for some of the desalter water requirement. The overall process water system is designed to have a normal operating holdup equivalent to 6-7 days of dry weather operation. The 2.4 million gallon oily water surge pond adds an additional holding capacity of one day ahead of the treatment system.

The initial treatment steps are primarily concerned with smoothing the rate of flow and the most efficient removal of oil. The oily water surge pond is available at the head of the system to limit flow rates to values within the capacities of the treatment equipment. The pH is controlled by metered injections of sulfuric acid and caustic soda based on values indicated by instruments continuously monitoring the pH. Two API separators, operating in parallel, remove floatable oil. In the forebay of the separators, first stage oil skimming is provided. The main bays of the separators are also fitted with skimmers, along with a sludge removal system. The skimmed oil is collected in a sump for recovery and re-use in the refinery. The sludge is de-oiled and de-watered for disposal. From the API separator the wastewater passes into the trickling filter.

The trickling filter makes up the first stage of the two stage biological treatment unit. Effluent from the API separators and a recycled flow from the filter itself are distributed over the media bed. The air supply is obtained by natural circulation. The effluent from the trickling filter is pumped into the aeration basin. This is the first half of the activated sludge unit. The effluent is aerated and mixed by three surface aerators and digested by the microorganisms present. The wastewater next flows into the clarifier for sedimentation of contaminants. Some of the clarifier contents are recycled to the aeration basin, while the clarified effluent passes on to a pair of clarification ponds which provide additional settling. Each pond has a capacity of 2.5 million gallons or more. The two earthern ponds may be utilized in parallel or series and minimize the solids content of the water entering the final holding pond. The effluent flows from the clarification pond through a baffled sluiceway to entrain air and increase the dissolved oxygen content, prior to discharge to the final holding pond and the outfall diffuser.

The sanitary water collection system carries wastes from all of the sanitary facilities within the refinery to a completely separate treatment plant. The system is designed with a 200% safety factor over the normal design criteria employed for municipal waste treatment facilities and can handle any potential peak flows. Physical treatment is supplied by a comminutor, which grinds up the wastes. An activated sludge unit, composed of an aeration basin and a clarifier, provides biological treatment. Two aerators supply the tank where the wastes are biologically consumed. The treated, clarified sanitary wastewater is then chlorinated for disinfection and discharged into the final holding pond with the rest of the refinery's treated wastewater effluent.

The final holding pond serves as equalization basin for peak flows and also provides an additional clarification of the effluent. The effluent is then pumped about 2 1/2 miles through pipe to the outfall diffuser. The diffuser lies under the refinery dock, over 2,100 feet offshore, 55 feet below the mean lower low water level of the Strait of Georgia. The diffuser is designed to mix the wastewater effluent in a ratio of one part effluent to 99-139 parts of seawater, effectively dispersing the effluent.

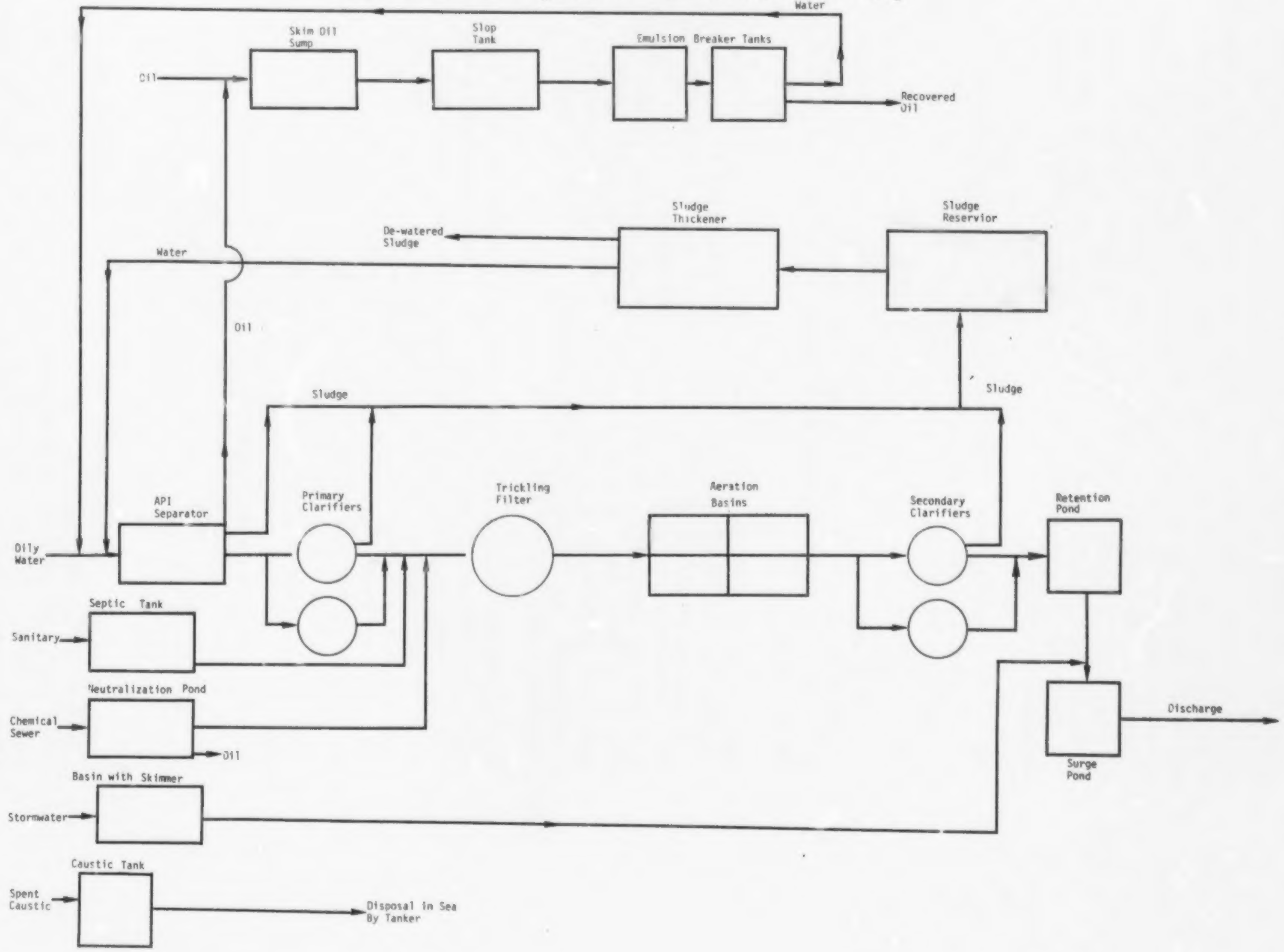
c. Shell. Shell's Anacortes refinery also has a large degree of complexity for dealing with the wastewater generated in the plant area and petroleum processes. Four major sewer systems handle the wastewater and deliver it to the treatment facility. These separate systems are: stormwater, chemical, sanitary and oily process water. Each system contains wastewater with various types and amounts of contaminants and receives different degrees of treatment to insure the most efficient removal of the contaminants (see Figure 18).

The stormwater sewer system collects all surface runoff from areas not subject to oil spillage. This uncontaminated water does not require biological treatment and simply undergoes physical treatment. The flow passes through a bar screen to remove trash and debris and then enters an oil skimming basin. The water is then discharged into the detention ponds, prior to release to the marine environment. The chemical sewer system receives dilute acid and caustic wash waters from the demineralizers used to soften the boiler feed water. These waters are held in a pond for neutralization and are used for pH control in the biological treatment processes. All of the sanitary wastes go to a large septic tank where bacteria digest the solid material present. The effluent from the septic tank is shock treated with acid for coliform control, then joins the oily water system prior to biological treatment.

The oily water sewer receives any water that is subject to possible oil contamination. It also receives the skimmed and steam stripped sour steam condensate from the boilers in the steam system. Process wash water is treated in-plant and is then routed to the oily water collection system. Cooling water

Figure 18

Wastewater Configuration at the Shell Refinery


Water
Skim Oil Sump
Slop Tank
Emulsion Breaker Tanks
Oil
Recovered Oil
Sludge Thickener
Sludge Reservior
De-watered Sludge
Water
Oil
Sludge
Sludge
API Separator
Primary Clarifiers
Trickling Filter
Aeration Basins
Secondary Clarifiers
Retention Pond
Oily Water
Septic Tank
Sanitary
Neutralization Pond
Chemical Sewer
Oil
Basin with Skimmer
Stormwater
Surge Pond
Discharge
Caustic Tank
Spent Caustic
Disposal in Sea By Tanker

which is recycled in the cooling towers and ballast water from tankers is processed in the oily water system. All precipitation and surface washing from the refinery process areas are also collected in the oily water sewers. All of these contaminated waterwaters receive extensive treatment, both physical and biological.

The oily water sewer empties into a two-channel API separator for oil removal. The floatable oils are skimmed off and sediments settle into the sludge handling system. The skimmed oil is collected in a sump where some of the water is removed and returned to the separator. Periodically the oil in the sump is passed on to the de-emulsifying tank and later to the slop oil collection tank for two stages of settling. Eventually the treated oil is returned to the refinery for reprocessing. The retention time of the wastewater in the API separator is about thirty-five minutes.

The skimmed water leaves the separator and passes on to the primary clarifiers, for initial sedimentation of suspended materials. The bottom sludge is removed frequently to maintain efficient settling. The pH is also adjusted at this stage, by the addition of waste dilute acid and caustic water. This aids flocculation and later biological treatment. After forty minutes, the wastewater leaves the clarifier and is joined by the effluent from the septic tank for biological treatment.

The water entering the biological treatment processes has diammonium phosphate added as a nutrient for the activated sludge. For fifteen minutes the wastewater is sprayed over the media bed of the trickling filter. This aerates the water enough to provide sufficient oxygen for the aerobic bacteria residing on the media. From the trickling filter the wastewater passes on to the aeration basin. The basin itself is divided into four large sections with a retention time of almost three hours. Jet nozzles aerate the basin, mixing the air, water and activated sludge to provide maximum treatment. The effluent from the aeration basin passes on to two final clarifiers. These remove activated sludge and allow remaining suspended solids to settle out. Thirty percent of the settled material is recycled to the activated sludge basin for additional treatment and maintenance of the biological culture. The remaining settled sludge is removed to the sludge handling system for later disposal.

After three and a half hours the treated effluent leaves the final clarifiers for two large detention ponds, with a total capacity of 11.5 million gallons. Over 96 percent of the BOD has been removed, 99.6 percent of the phenols, 100 percent of the sulfides, around 99 percent of the oil and an oxygen residual of 7.5 ppm is established after the final treatment processes. In the detention ponds the treated effluent is joined by skimmed stormwater and analyzed for its water quality.

If necessary the water is returned to the plant for additional treatment. Otherwise the basin water passes through a hay filter and is discharged into the bay 34 feet below low mean tide during outgoing tides, to insure rapid dispersion of the effluent.

Spent caustic containing around 15 percent NaOH is separated and stored in a tank for later chemical recovery. Lower strength caustic, usually less than 2 percent NaOH, is separated and is either passed through the treatment plant or is disposed of at sea. Sludge is collected from the API separator, primary clarifiers and the final clarifier for treatment and disposal. The sludge is dewatered, filtered and incinerated.

d. Texaco. Wastewater at Texaco's March Point refinery is separated into three sewer collection systems (see Figure 19). The stormwater sewers receive water from boiler and steam generator blowdown, backwash from the softening equipment and plant surface runoff, all of which are relatively uncontaminated. Ballast water from incoming vessels is collected in the ballast water system. The process water sewers collect contaminated water from the sour water strippers, cooling tower blowdown, sanitary wastewater and other contaminants which have been neutralized prior to release to the system.

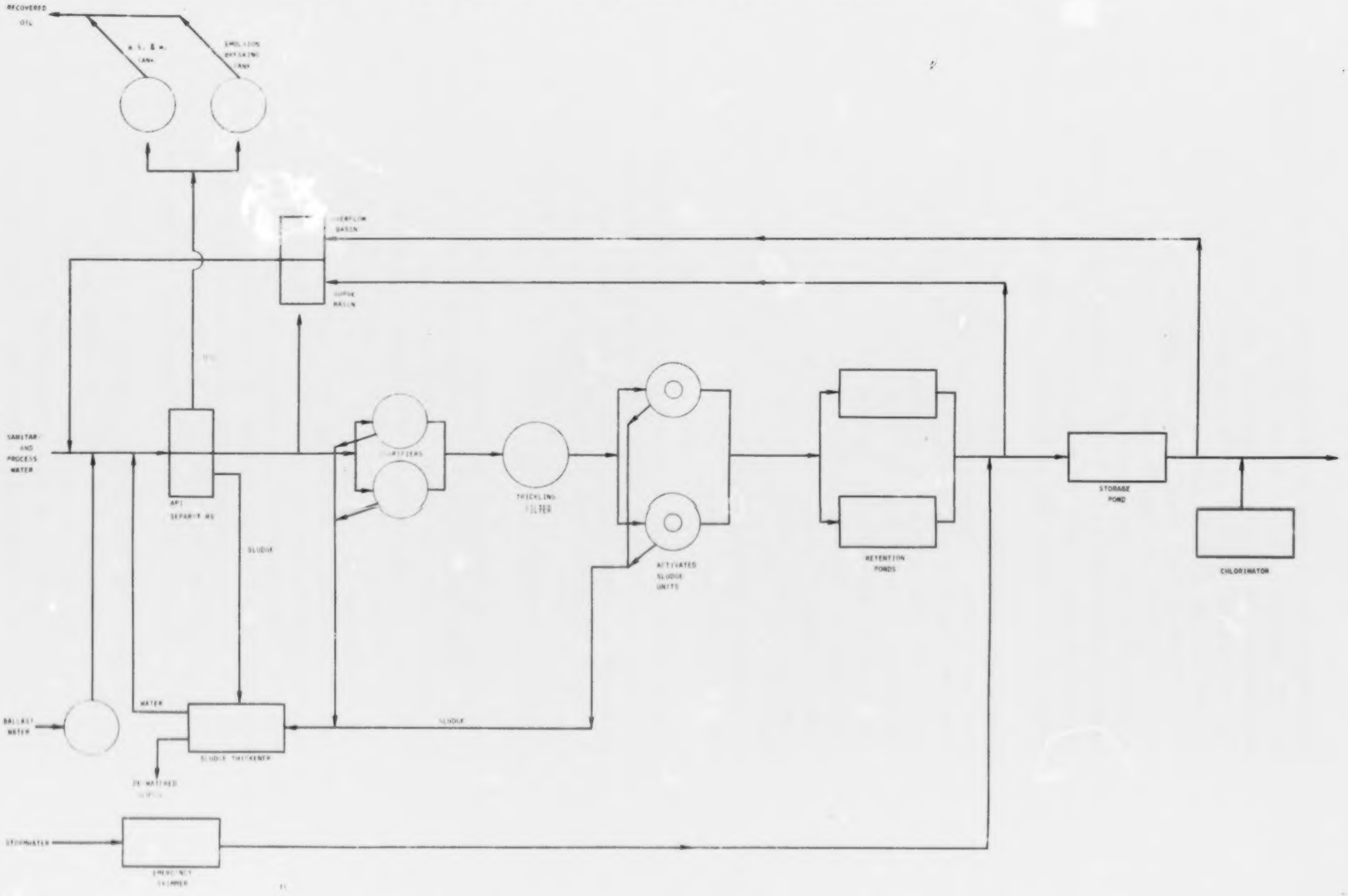
The uncontaminated waters in the stormwater system receive relatively simple treatment. A flume is used for trash removal and an emergency oil skimmer is used to remove any oil that might be present. The water then passes on to a 7.5 million gallon storage pond prior to chlorination and final discharge. Ballast water is released to the process water system or to the stormwater sewers depending on the degree of treatment required.

All of the contaminated wastewater at the refinery is collected in the process water sewers and receives extensive treatment. The first treatment process is a two-bay API separator. It is designed to handle peak flows and provides oil and sediment removal. The sludge collected is periodically removed for further treatment. The skimmed oil is pumped to the bottom sediment and water (BS & W) tank for oil recovery and subsequent reuse in the refinery. The discharge from the API separator goes to the chemical clarifiers. A 0.12 million gallon surge basin is available, along with a 2.2 million gallon overflow basin, to handle any excessive peak or heavy flows. Lime, alum and activated silica are normally added in the two clarifiers to assist coagulation and sedimentation of suspended material. Settled sludge is removed and pumped to the sludge thickener for further treatment, while oily water skimmed from the surface is returned to the API separator for more efficient oil removal.

Biological treatment of the wastewater is accomplished in two stages. The effluent from the clarifier flows to a trickling filter. Here, bacteria serve to remove organic material from

Figure 19

Wastewater Treatment Configuration at the Texaco Refinery


RECOVERED OIL
B.S. & W. TANK
EMULSION BREAKING TANK
OVERFLOW BASIN
SURGE BASIN
OIL
SANITARY AND PROCESS WATER
API SEPARATORS
SLUDGE
CLARIFIERS
TRICKLING FILTER
ACTIVATED SLUDGE UNITS
RETENTION PONDS
STORAGE POND
CHLORINATOR
BALLAST WATER
WATER
SLUDGE THICKENER
DE-WATERED SLUDGE
SLUDGE
STORMWATER
EMERGENCY SKIMMER

the water as it passes through the media bed. Oxygen is supplied by the natural circulation of air through the filter bed. The wastewater is usually recycled over the bed at least three times. Two activated sludge units, operating in parallel, serve as the second stage of biological treatment. The units are different from conventional activated sludge units in that the aeration and clarification are performed in a single unit. Here again, microbiological organisms are used to treat the wastewater and remove contaminants. During periods when nutrients are low in the wastewater, ammonium phosphate is fed ahead of the biological units to maintain the organisms in the two treatment processes.

Discharge from the activated sludge units passes on to two retention ponds. These serve two major functions; continued oxidation of phenols and isolation of the wastewater in case an upset occurs in the treatment system and retreatment is necessary. The water is retained in these ponds for about twelve hours. The treated wastewater passes on to the storage pond, where it is joined by the uncontaminated storm and ballast water. In case of heavy flows, the treated water can be shunted to the overflow and surge basins. From the storage pond the treated effluent flows through a hay filter to remove any remaining oil and is chlorinated automatically prior to disposal at the refinery dock during outgoing tides.

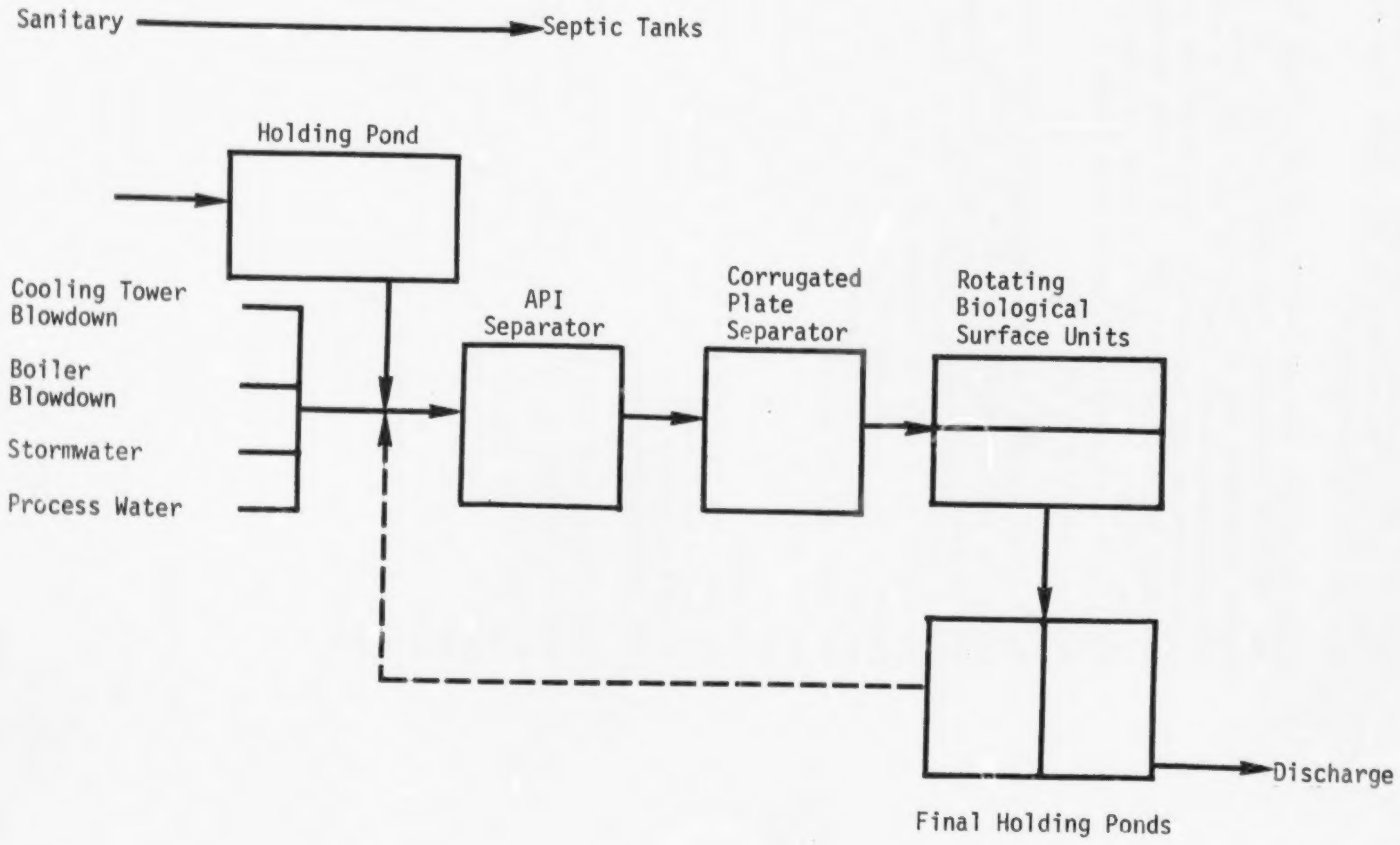
Sludge from various treatment units is thickened and filtered, with the resulting sludge cake being incinerated. Oil from the separators, from the ballast water tank and slop oil from the refinery is collected in the emulsion-breaking and BS & W tanks for oil recovery. Spent caustics are collected and regularly pumped to a petrochemical plant for processing.

e. U.S. Oil & Refining. Wastewater from cooling tower blowdown, boiler blowdown, asphalt process cooling water overflow system, equipment cleaning water, process waters and stormwater are received by the wastewater treatment system at the U.S. Oil & Refining refinery. These are collected in a single sewer system and delivered to the head of the wastewater treatment system (see Figure 20). Drainage from tank areas enters a temporary holding pond prior to entering the treatment processes. At the present time sanitary wastewater is handled by septic tanks. When the local sewer system is expanded, the refinery will tie into it, in accordance with state permits. The sanitary facilities at the refinery dock are already tied in to the sewer system. No ballast water is received by the refinery from ships.

Wastewater from the process areas is all treated with emulsion breaking chemicals and heat to enhance oil removal prior to entering the API separators for seven hours for removal of oil and particulates. A new corrugated plate separator is the next step of wastewater treatment. This removes more oil, then the water passes on to two rotating biological surface (RBS) units where BOD is reduced and phenols are removed. The effluent

Figure 20

Wastewater Treatment Configuration at the U.S. Oil and Refining Refinery


Sanitary
Septic Tanks
Holding Pond
Cooling Tower Blowdown
Boiler Blowdown
Stormwater
Process Water
API Separator
Corrugated Plate Separator
Rotating Biological Surface Units
Final Holding Ponds
Discharge

from these biological treatment units is clarified in two ponds used as settling and holding ponds prior to discharge of the final effluent into Blair Waterway. Water in these ponds can also be returned to the head of the system should further treatment be considered necessary.

f. Sound Refining. The wastewater treatment plant for Sound Refining, Inc. receives wastewater from process areas, loading racks, storm drains throughout the refinery and all tank area drains. Sanitary wastewater is not treated at the refinery site; instead it is collected in the Tacoma sewer system and treated by the city's municipal waste treatment plant. All other wastewater generated at the refinery is collected in a single system and is treated identically, regardless of source (see Figure 21). No ballast water is received from ships.

The initial step of the treatment system is a holding pond into which the various wastewaters flow by gravity. A portion of the holding pond is divided into two separating chambers in which oil is removed from the wastewater. The oil removed is collected and stored in a tank for further treatment. The wastewater passes on to the API separator, where additional oil removal occurs. This oil is also collected in a small storage tank. The recovered oil is heated to a low temperature for more oil and water separation. The water from this procedure is returned to the API separator for continued treatment with the rest of the wastewater. The oil recovered in the storage tank is moved to another area for further separation and is eventually returned to the crude storage tanks for reprocessing. The effluent from the API separator passes through a straw filter and is discharged into Hylebos Waterway.

The refinery had been considering the addition of biological treatment in the form of rotating biological surface units and polisher units (providing final clarification). But a change in management has halted the upgrading of the refinery wastewater treatment methods. Potential changes in the refinery operations under the new management will delay the addition of new treatment processes. Consideration is being given to aerating the existing pond, adding a corrugated plate API separator, rotating biological surface units and a final clarifier to remove biological sludge, but no definite plans have been made.

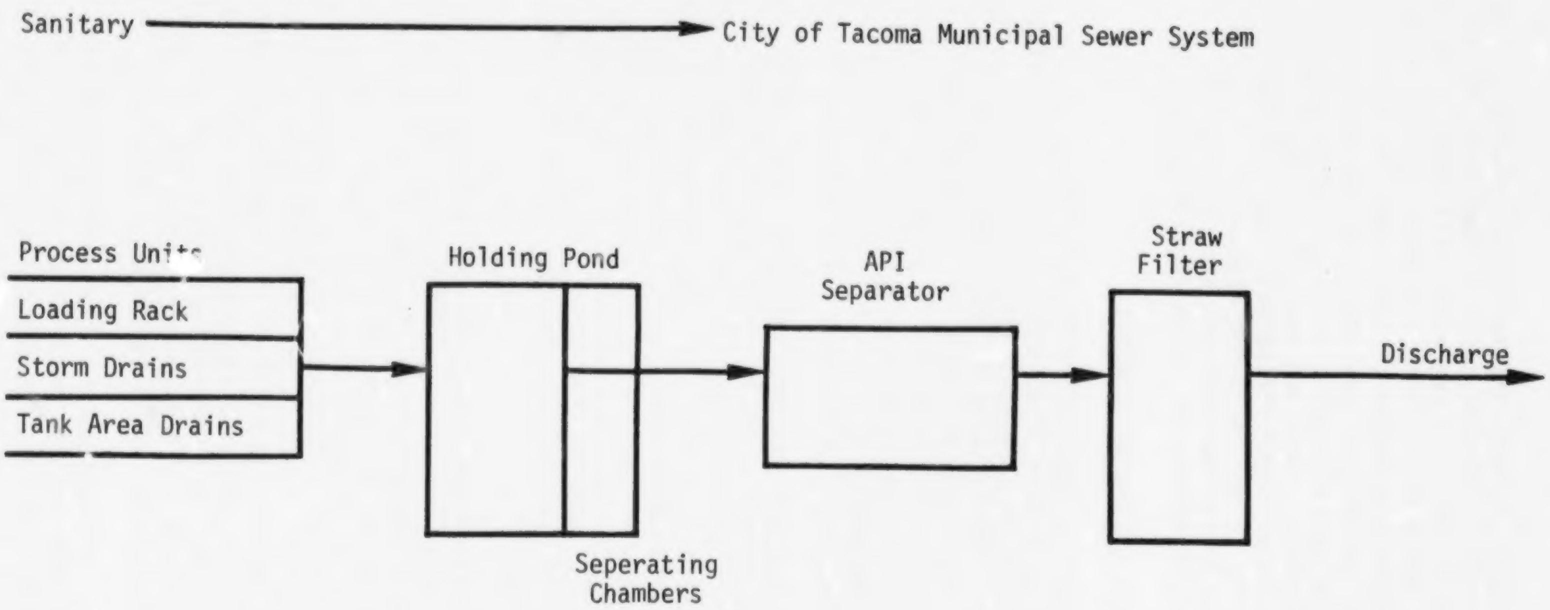
H. Refinery Wastewater Effluent Characteristics

1. Introduction.

The final treated effluent discharge from refineries still contains a wide variety of chemical constituents and characteristics, despite the highly efficient wastewater treatment processes employed. It is virtually impossible for a treatment plant, utilizing physical and biological treat-

Figure 21

Wastewater Treatment Configuration at the Sound Refining Refinery


Sanitary
City of Tacoma Municipal Sewer System
Process Units
Loading Rack
Storm Drains
Tank Area Drains
Holding Pond
Seperating Chambers
API Separator
Straw Filter
Discharge

ment processes (primary and secondary treatment), to eliminate completely the particular pollutants arising from crude oil refining operations. Even the most efficient processes will leave a low level concentration of pollutants which will affect the water quality of the marine receiving waters. Because a number of these chemical constituents may contribute a significant quantity of pollutants to the marine environment, regulations exist governing permissable levels of these parameters. Table 54 contains a relatively detailed analysis of the effluent characteristics from one of the Puget Sound refineries. Such in-depth reporting of effluent water quality is not performed regularly. Each refinery is responsible for monitoring its own effluent discharge and is principally concerned with those parameters for which regulations exist.

2. Effluent Discharge Permits.

Regulations regarding allowable levels of specific water quality parameters are contained in National Pollutant Discharge Elimination System (NPDES) discharge permits issued every three to five years to individual refineries. The issuance of these NPDES permits formerly was handled by the U. S. Army Corps of Engineers and is now under the control of the Washington State Department of Ecology. Permit allocation levels for specific pollutants in petroleum refinery wastewater effluent are established in accordance with the refinery effluent limitation guidelines developed and promulgated by EPA's Office of Air and Water Programs.

The Petroleum Industry Raw Waste Load Survey of 1972 (EPA/API Raw Waste Load Survey) (10) was instrumental in the formulation of these guidelines. Approximately 135 refineries nationwide were surveyed during the 1972 study. In addition, five refineries utilizing activated sludge treatment units were subjected to intensive sampling for identification of wastewater treatment plant effluent performance. Five refineries in the state of Washington (Sound Refining was not involved) were included in the overall survey and the Shell refinery was subjected to an intensive examination of its wastewater treatment processes (which includes an activated sludge unit).

Table 55 presents the data collected by the EPA survey team during March and April of 1972 at the five Washington State refineries. Refineries are classed by EPA according to the type of refining processes they employ. Simple refineries which do not involve cracking processes, such as U.S. Oil & Refining, are categorized as class "A" or "topping" refineries. Those non-petrochemical refineries utilizing cracking processes are labeled class "B" refineries. Table 56 presents the results of the 14-day data and sample collection and analyses of composite effluent samples from the Shell refinery. This analysis shows pollutant levels after each of three treatment processes: API separator, trickling filter, and activated sludge. Minimum, average and maximum concentrations (in mg/l) are given, along with the percent removal efficiency of the collective treatment processes.

Permit allocations are developed for each parameter on the basis of the results of this survey, established toxicity levels for a particular pollutant, the type of refining processes involved and the volume of the effluent

Table 54

Effluent Discharge Water Quality from a Puget Sound Refinery

	Ave.	Max.
pH	6.5 - 8.5	6.0 - 9.0
Temperature	70-75 °F	60-80 °F
Phenols, ppm	0.4	3.8 (Norm. Max. 1.0)
Total Oils, ppm	5-10	15
Sulfides, ppm	0	1
Mercaptans, ppm	0	0.5
Total Chromium, ppm	0.1	0.5

From Single Sampling

Alkalinity (as $CaCO_3$), ppm	33
BOD 5-day, ppm	84
COD, ppm	10
Total Solids, ppm	600
Total Dissolved Solids, ppm	545
Total Suspended Solids, ppm	31
Total Volatile Solids, ppm	65
Ammonia, ppm	4.25
Kjeldahl Nitrogen, ppm	6.4
Nitrate, ppm	1.52
Phosphorus, Total, ppm	0.01
Color, Pt-Co Units	4.5
Turbidity, Jackson Units	17
Total Organic Carbon, ppm	79
Total Hardness, ppm	104
Organic Nitrogen, ppm	3
Sulfate, ppm	38
Chloride, ppm	438
Cyanide, ppm	<0.01
Fluoride, ppm	6
Aluminum-Total, ppb	400
Arsenic-Total, ppb	<1
Cadmium-otal, ppb	<1
Calcium-Total, ppm	56
Copper-Total, ppb	48
Iron-Total, ppb	2000
Lead-Total, ppb	<15
Nickel-Total, ppb	<50

Table 54 (cont.)

Potassium-Total, ppm	13
Sodium-Total, ppm	95
Zinc-Total, ppb	47
Fecal Streptococci Bacteria/100ml	270
Total Coliform Bacteria/100ml	52,000

PARAMETER	CLASS A: REFINERIES	CLASS B REFINERIES:				NATIONAL AVERAGES (MEDIAN VALUES)	
	U.S. Oil & Refining	ARCO	Mobil	Shell	Texaco	CLASS A REFINERIES	CLASS B REFINERIES
Crude Capacity (thousand barrels/day)	20.0	100.0	58.4	90.0	65.0	---	---
Crude Capacity on Day of Sampling (thousand barrels/day)	24.5	90.0	63.9	87.0	66.18	---	---
Water Discharged (million gallons/day)	0.9	1.4	1.20	2.2	2.88	---	---
Gallons of Water Discharged per Barrel of Crude	3.67	15.56	18.78	25.3	43.5	18.0	40.44
BOD[5]	1.43	16.2	10.2	29.5	20.2	2.9	38.29
COD	3.37	25.5	105.0	135.7	135.5	13.3	105.8
TOC	1.36	---	---	6.11	12.5	2.5	17.8
Oil & Grease	1.21	6.18	9.5	11.9	3.7	3.13	13.8
Phenols	0.1	0.00	4.4	1.5	1.4	.01	1.5
Suspended Solids	3.9	2.6	18.8	3.9	2.37	4.4	11.8
Dissolved Solids	16.3	133.7	51.1	345.6	195.2	103.5	210.7
Sulfides	.03	0.26	---	2.99	.07	.03	.34
Hexavalent Chromium	0.00	0.00	0.00	.10	.02	0.00	.03
Ammonia	.01	.16	2.63	.15	82.02	.34	7.8
Organic Nitrogen	.04	.18	6.32	21.7	11.45	.04	2.4
Nitrate Nitrogen	0.00	.24	3.69	.14	.40	.01	0.00
Acidity	.92	1.75	0.00	0.00	10.1	.96	0.00
Alkalinity	3.06	3.85	4.27	41.8	126.1	.53	12.4
Phosphates	.04	.33	.08	.03	.3	.02	.08
Cyanide	0.00	---	.23	0.00	2.25	.00	.00
Chloride	4.07	52.9	32.60	127.00	60.24	15.75	65.34
Iron	.06	.04	---	.06	.5	.06	.22
Copper	0.00	0.00	---	.01	.01	0.00	.22
Lead	0.00	.02	---	0.00	.22	0.00	0.00
Zinc	0.00	.027	---	.01	.01	0.0	.07

Source: (10)

Table 55

1972 Data Collected in the
EPA/API Raw Waste Load Survey
on Five Puget Sound Refineries

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[5] Units for all chemical parameters are mg/l.

Effluent Parameters	Wastewater Treatment Processes			Percent Removal Efficiency
	API Separator§	Trickling Filter§	Activated Sludge§	
BOD	70-83-228	38-47-69	16-19-26	77.7%
COD	191-243-583	154-184-411	102-130-201	44.7%
TOC	44-57-180	42-49-112	29-37-62	33.0%
Oil and Grease	16-31-60	12-23-45	9.0-17-31	44.8%
Suspended Solids	19-56-261	25-39-66	6.0-25-83	58.1%
Dissolved Solids	1050-1490-1860	1230-1590-1840	1370-1615-1820	-17.7%
Sulfides	17-24.3-31	.00-.75-4.8	.00-.275-.8	98.7%
Hexayalent Chromium	1.5-1.8-2.6	0.9-1.3-2.7	.18-.5-.9	73.0%
Ammonia	98-127-160	89-108-140	84-106-124	16.5%
Organic Nitrogen	.05-2.8-46.9	.05-5.4-36.1	.05-6.0-26.0	22.7%
Nitrate Nitrogen	.03-.48-.95	.4-.53-.75	.28-.38-.61	17.5%
Acidity	.00-.00-.00	.00-.00-22	.00-.00-26	0.0%
Alkalinity	575-708-820	158-201.5-340	166-191-227	72.2%
Phenols	7.5-10.5-16	.44-.99-2.6	.02-.035-.47	99.6%
Phosphates	.03-.16-.57	.22-.3-.9	0.09-.16-.36	-1.4%
Cyanide	1.2-1.5-2.5	.17-.25-.62	.06-.07-.280	95.1%
Chloride	374-556-796	333-431-650	334-409-616	19.2%
Iron	.5-.97-44	1.0-1.5-28.5	.44-.88-1.4	36.6%
Copper	.02-.03-.05	0.02-.03-.03	.02-.03-.045	00.0%
Lead	.00-.1-.2	.03-.11-.18	.09-.11-.16	-12.4%
Zinc	.13-.22-.82	.16-.29-1.24	.07-.16-1.84	22.0%

Source: (10)

§Values are listed in the following order: minimum, average and maximum (in mg/l)

Table 56

1972 Data Collected in the EPA/API Raw Waste
Load Survey on Wastewater Treatment Processes
Used at the Shell Refinery

discharge. Each wastewater constituent which is considered to be harmful is assigned an average and maximum level which is not to be exceeded in the refinery effluent. Additional pollutant allocations are based on the ballast and stormwater flows. Specific factors have been established for certain water quality parameters (usually total suspended solids, biological oxygen demand, chemical oxygen demand and oil and grease), which are then multiplied by the volume of ballast and stormwater flows to yield the additional allowable levels of pollutants in the refinery effluent discharge.

The parameters considered to be important by the state have been modified and expanded within the past few years, and the new pollutant allocations have been incorporated as the old permits expired and new ones were issued. In the past, the parameters monitored in accordance with the NPDES discharge permits included:

- Oil and Grease
- pH
- Sulfide
- Phenols
- Mercaptans
- Hexavalent Chromium

Sound Refining and U.S. Oil & Refining were exempted from reporting levels of mercaptans. The new permits require that the following parameters are monitored:

- Oil and Grease
- Total Suspended Solids (TSS)
- Ammonia (as Nitrogen)
- pH
- Sulfide
- Chemical Oxygen Demand (COD)
- Biological Oxygen Demand (BOD)
- Phenolic Compounds
- Hexavalent Chromium
- Total Chromium

- Fecal Coliform
- Temperature
- Discharge Rate

Some of these parameters have gone unreported in the recent past; however, modifications to the discharge permits in 1976 now assure the monitoring of each parameter by Mobil, ARCO, Shell and Texaco. U.S. Oil & Refining is also responsible for all of these parameters with the exception of temperature and fecal coliform. The quantity of oil and grease is not always reported; however, it can be calculated from the reported concentration and the discharge rate. Sound Refining is the smallest refinery and is essentially just a topping refinery--the crude oil is distilled with very little additional processing. Hence it is not responsible for all the same water quality parameters that the larger, more complex refineries are.

In addition to changes concerning which parameters are measured, the method of reporting pollutant levels has been altered. Prior to 1975, permit allocations were totally concerned with the concentration of the various pollutants. These were reported in mg/l. Since that time, emphasis has shifted towards limiting the total amount of each pollutant discharged by a refinery each day. The newly issued permits call for parameters to be reported in pounds per day. Oil and grease is the only parameter for which a concentration is also reported.

The NPDES discharge permits require each refinery to report the level of pollutants measured in the refinery effluent at the end of each month. Occasional spot-checks are made by representatives of the Department of Ecology to ensure proper reporting of pollutant quantities. Tables 57, 58, 59, 60, 61, and 62 are summaries of the annual average and maximum levels of pollutants for 1974, 1975, and 1976 in the effluent discharge from each of the six Puget Sound refineries. Monthly average and maximum levels for 1974, 1975, and 1976, as reported in accordance with individual discharge permits, are in tables in Appendix C.

3. Toxic Effluent Pollutants.

Five major harmful pollutants can be found in the effluent discharge from petroleum refineries. These are phenols, sulfides, mercaptans, hexavalent chromium, and oil. Phenols and phenolic compounds are both acutely and chronically toxic to fish and other marine organisms. Many phenolic compounds are more toxic than pure phenol, depending on which combinations of compounds are present in the effluent. Phenols and phenolic compounds have been reported to be toxic under some circumstances in concentrations ranging from 1.0 to 10.0 mg/l. Lower concentrations may not be lethal, but impart an unpleasant taste to fish flesh (tainting), destroying its recreational and commercial value.

When present in water, sulfides can reduce pH, react with metallic compounds forming precipitates, cause odor problems, and can be toxic to marine life. The toxicity of sulfides increases as the pH decreases.

Table 57

Summary of Annual Levels of Pollutants Present in the Wastewater Effluent of the Mobil Refinery[§]

Parameter	1974		1975		1976	
	Average	Maximum	Average	Maximum	Average	Maximum
Oil and Grease (conc.)	12.9	147†	8.1	26†	6.2	10
(quant.)	108	1074	71	450	80	220
Total Suspended Solids	27	780	266	1800	210	796†
Ammonia (as Nitrogen)	0.8	2.9	7.2	22	5.2	27
pH	4.0	8.6	6.9	8.5	6.8	7.7
Sulfide	0	0	0	0	0	0
Chemical Oxygen Demand	167	1040	829	2250	1097	4400†
Biological Oxygen Demand	52	426	179	680	111	340
Phenolic Compounds	0.19	2.5†	1.04†	6.4†	0.89	6.2†
Hexavalent Chromium	<0.01	0.11	0.02	6.9	0.01	0.24†
Total Chromium	0.04†	0.29†	0.51†	2.7†	0.52	2.72
Fecal Coliform	5978	32000	2018	35000	206	700
Temperature	76	92	64	80	55	70
Discharge Rate	1.01	2.71	1.08	3.51	1.36	2.93

Source: (35)

[†] Exceeded appropriate permit levels

[§] For 1974 all units are in mg/l and for 1975-1976 all units are in lbs/day, except; pH (in pH units), temperature in ^{O}F), fecal coliform (in most probable number/100 ml) and discharge rate (in million gallons per day). Oil and grease concentration is reported in mg/l. Also pH is given as minimum and maximum, with no average value.

Table 58

Summary of Annual Levels of Pollutants Present in the Wastewater Effluent of the Arco Refinery[§]

Parameter	1974		1975		1976	
	Average	Maximum	Average	Maximum	Average	Maximum
Oil and Grease (conc.)	2.1	5	-	10.1	-	11.0
(quant.)	-	-	50	276	55	345
Total Suspended Solids	-	-	459	2665	288	1637
Ammonia (as Nitrogen)	-	-	118	884	21	225
pH	6.4	8.6	5.9	8.8	6.5	8.4
Sulfide	<0.1	<0.1	0	0	0	0
Chemical Oxygen Demand	-	-	659	4017	404	4023
Biological Oxygen Demand	-	-	256	1313	187	949
Phenolic Compounds	<0.1	<0.1	0	0	0	0
Hexavalent Chromium	<0.02	<0.02	0	0	0	0
Total Chromium	-	-	0	0	0	0
Fecal Coliform	-	-	0	0	0	0
Temperature	-	-	46	62	51	73
Discharge Rate	2.38	7.64	4.07	9.1	2.08	5.32

Source: (34)

[§] For 1974 all units are in mg/l and for 1975-1976 all units are in lbs/day, except; pH (in pH units), temperature (in °F), fecal coliform (in most probable number/100 ml) and discharge rate (in million gallons per day). Oil and grease concentration is reported in mg/l. Also pH and temperature are given as minimum and maximum, with no average value.

Table 59

Summary of Annual Levels of Pollutants Present in the Wastewater Effluent of the Shell Refinery[§]

Parameter	1974		1975		1976	
	Average	Maximum	Average	Maximum	Average	Maximum
Oil and Grease (conc.)	2.3	7.	1.2	6	1.1	2
(quant.)	-	-	20	304	19.6	60
Total Suspended Solids	-	-	214	2752	280	1970
Ammonia (as Nitrogen)	-	-	1330	5000[†]	1314	5540[†]
pH	6.5	8.1	6.4	9.0	6.0	8.6
Sulfide	<0.1	<0.1	< 0.1	< 0.1	< 0.1	< 0.1
Chemical Oxygen Demand	-	-	3537	16394	3882	14900
Biological Oxygen Demand	-	-	291	1130	345	1100
Phenolic Compounds	0.06	0.14	0.51	5.60	0.50	4.15
Hexavalent Chromium	0.005	0.06	0.08	0.33	0.07	0.36
Total Chromium	-	-	0.79	3.19	0.71	2.70
Fecal Coliform	-	-	42	382	29	200
Temperature	-	-	63	81	58	79
Discharge Rate	1.85	12.60	1.99	9.70	2.08	7.20

Source: (36)

[§] For 1974 all units are in mg/l and for 1976-1976 all units are in lbs/day, except; pH (in pH units), temperature (in ^{O}F), fecal coliform (in most probable number/100 ml) and discharge rate (in million gallons per day). Oil and grease concentration is reported in mg/l. Also pH is given as minimum and maximum, with no average value.

[†] Exceeded approriate permit levels

Table 60

Summary of Annual Levels of Pollutants Present in the Wastewater Effluent of the Texaco Refinery[§]

Parameter	1974		1975		1976	
	Average	Maximum	Average	Maximum	Average	Maximum
Oil and Grease (conc.)	4.8	15	2.6	12	2.8	10
(quant.)	-	-	66	496†	70	238
Total Suspended Solids	-	-	423	6276†	327	2015†
Ammonia (as Nitrogen)	-	-	970	3609†	187	1303
pH	6.5	10.5†	6.3	9.0	6.0	11.7†
Sulfide	<0.1	<0.1	0.4	5.1	0.4	5.2†
Chemical Oxygen Demand	-	-	1910	11556	1443	4714
Biological Oxygen Demand	-	-	195	1565	161	2549†
Phenolic Compounds	0.12	2.0†	1.6	10.8†	1.5	35.0†
Hexavalent Chromium	<0.1	0.2†	0.1	1.9	< 0.1	1.3†
Total Chromium	-	-	3.9	13.1	3.2	19.2†
Fecal Coliform	-	-	490†	2100†	0	10
Temperature	-	-	53	85	55	77
Discharge Rate	3.41	12.38	2.93	4.31	2.94	-

Source: (38)

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†Exceeded appropriate permit levels

§For 1974 all units are in mg/l and for 1975-1976 all units are in lbs/day, except; pH (in pH units), temperature (in °F), fecal coliform (in most probable number/100 ml) and discharge rate (in million gallons per day). Oil and grease concentration is reported in mg/l. Also pH and temperature are given as minimum and maximum, with no average value.

Table 61

Summary of Annual Levels of Pollutants Present in the Wastewater Effluent of U.S. Oil & Refining[§]

Parameter	1974		1975		1976	
	Average	Maximum	Average	Maximum	Average	Maximum
Oil and Grease (conc.)	13.1	38.8	13.9	39.7[†]	13.8[†]	38.6[†]
(quant.)	-	-	-	-	-	-
Total Suspended Solids	-	-	61.7	122.7	32.8	46.2
Ammonia (as Nitrogen)	-	-	2.1	2.1	1.6	3.4
pH	6.5	8.0	6.5	8.3	6.5	8.1
Sulfide	< 0.1	0.1	0.11	0.18	0.14	0.16
Chemical Oxygen Demand	-	-	117	229	107	170
Biological Oxygen Demand	-	-	63	126	40	95
Phenolic Compounds	0.64	1.73	0.27	1.13	0.31	1.35[†]
Hexavalent Chromium	-	-	< 0.015	< 0.015	0.013	0.015
Total Chromium	-	-	0.25	0.25	0.49	1.14
Fecal Coliform	-	-	-	-	-	-
Temperature	-	-	-	-	-	-
Discharge Rate	0.16	0.18	0.16	0.22	0.17	0.19

Source: (39)

[†] Exceeded appropriate permit levels

[§] All units for 1974 and 1975 (except December 1975) are in mg/l and for 1976 (including December 1975) all units are in lbs/day, except; pH (in pH units) and discharge rate (in thousand gallons per day). Also pH is given as minimum and maximum, with no average value.

Table 62

Summary of Annual Levels of Pollutants Present in the Wastewater Effluent of the Sound Refining Refinery[§]

Parameter	1974		1975		1976	
	Average	Maximum	Average	Maximum	Average	Maximum
Oil and grease	5.5	11.8	6.1	32.6[†]	3.9	12.0
pH	6.7	8.4	6.8	8.2	-	-
Sulfide	0.2	0.5	0.3	1.4[†]	0.2	0.6
Phenols	0.35	0.86	0.41	1.2	0.26	0.92
Chemical Oxygen Demand	-	-	195	-	123	-
Biological Oxygen Demand	-	-	39	-	37	-
Discharge Rate	47.8	99.4	41.4	99.4	36.4	107.8

Source: (37)

[†] Exceeded permit levels

[§] All units are in mg/l, except; pH (in pH units) and discharge rate (in thousand gallons per day). Also pH is given as minimum and maximum, with no average value.

Studies have shown that sulfide concentrations of 1.0-6.0 mg/l are toxic to some species of fish. Mercaptans also lower the pH of the receiving waters and cause extreme odor problems. Toxicity levels for mercaptans have been found to be as low as 1.0-2.0 mg/l in some studies.

Chromium may exist in refinery effluent in both the hexavalent and trivalent state. The toxicity of chromium salts to marine organisms varies greatly with the individual species, temperature, pH and specific interactions with other water characteristics, particularly hardness. Hexavalent chromium is the more toxic form of the chromium oxidation states. Fish are relatively tolerant of chromium salts, but fish food organisms and other forms of marine life are extremely sensitive. Marine planktonic algae are also inhibited by hexavalent chromium. Generally, toxic levels of hexavalent chromium are 5.0 mg/l or less.

Oil and grease compounds make their presence felt in the COD and BOD because of the oxygen demand of these hydrocarbon compounds. Oil emulsions adhere to the gills of fish or coat algae and other plankton, causing death. Deposition of effluent oil content in the bottom sediments can adversely affect benthic organisms and habitats. The water insoluble components may exert toxic action on fish and other species, at concentrations ranging from 1.0-20 mg/l depending on the exact composition of the oil and grease fraction.

No breakdown of this oil and grease measurement into specific hydrocarbons or hydrocarbon classes is performed. The refineries are not required to monitor specific hydrocarbons, and the state agencies do not make a detailed analysis of the oil and grease constituents when they spot-check the refinery effluent. The standard analysis for oil and grease was developed as a gross measure of potential water quality and sanitary engineering problems. Originally, it was aimed at assessing the quantities of animal fats and oils in municipal wastewater. The test is based on solvent extraction by use of an organic solvent, such as hexane, petroleum ether, carbon tetrachloride, chloroform, benzene or freon, and is predominantly for determining grease content. The analysis is further complicated by the fact that low-boiling fractions are lost in the usual oil and grease analysis. For example, kerosene and gasoline content cannot be determined by the normal petroleum ether extraction method which is used for measurements in natural waters, and is the most common method used by the refineries. Thus, the accuracy of the report values for oil and grease content in refinery effluent discharges is not necessarily high and probably does not reflect the actual hydrocarbon content.

The effects of refinery effluents depend on many factors other than the obvious ones of effluent constituents and volume. The siting of the outfall, the type of receiving area (rock, mud, sand or saltmarsh) and its associated community of plants and animals, and the movements and quality of the receiving water all must be considered. Different ecosystems differ in their capacity to receive and degrade effluents, and the speed of dispersion and dilution is a major factor determining the amount of biological damage. Changes in distribution and abundance of species are often very localized and in some cases may result from behavioral responses rather than direct toxic effects. Most undiluted refinery effluents can be shown to be harmful in the long term; however, they are not usually acutely toxic. They can cause sub-lethal effects such as changes in metabolic rate or behavior. Such effects over a long period of time may help to explain population changes near effluent discharges.

Bioassays utilizing undiluted effluent and water samples from the area of discharge have been performed since 1971 by the Washington Department of Fisheries and in recent years by the refineries themselves. These have yielded widely variable results, although most frequently there have been no indications of lethality to the test organisms (Coho and Chinook salmon and oyster embryos). However, it should be noted that the refinery effluents constitute a chronic discharge of hydrocarbons, regardless of the fact that oil removal efficiencies of different refinery wastewater treatments plants range from 95 to 99.99 percent. Most of these wastewater treatment processes are not effective in removing soluble hydrocarbons, particularly aromatics. Thus, an apparently efficient system which reduces the total oil content to as little as 5-20 mg/l could still contain greater than 1.0 mg/l of soluble aromatic hydrocarbons, a sufficient concentration to cause sub-lethal effects and, for the most sensitive organisms, direct lethal effects. Tables 63, 64, 65, 66, 67, and 68 are summaries of the annual average and maximum levels of these five toxic pollutants which are present in the wastewater discharges from the six Puget Sound refineries.

Table 63

Summary of the Annual Levels of Toxic Pollutants Present in the Wastewater Effluent at the Mobil Refinery

Parameter	1974		1975		1976	
	Average	Maximum	Average	Maximum	Average	Maximum
Oil and Grease (conc.)	12.9	147	8.1	26	6.2	10
(quant.)	108	1074	71	450	80	220
Phenols	1.63	16.8†	1.04	6.4†	0.89	6.2†
Sulfides	0	0	0	0	0	0
Mercaptans	0	0	0	0	0	0
Hexavalent Chromium	0.02	0.78†	0.02	6.9†	0.01	0.24†

†Exceeded NPDES permit levels.
All units are in lbs/day, except oil and grease concentrations (mg/l).

Table 64

Summary of the Annual Levels of Toxic Pollutants Present in the Wastewater Effluent of the ARCO Refinery

Parameter	1974		1975		1976	
	Average	Maximum	Average	Maximum	Average	Maximum
Oil and Grease (conc.)	2.1	5	§	10.1	§	11.0
(quant.)	§	§	50	276	55	345
Phenols	<0.1	<0.1	0	0	0	0
Sulfides	<0.1	<0.1	0	0	0	0
Mercaptans	<0.1	3.2	§	§	§	§
Hexavalent Chromium	<0.02	<0.02	0	0	0	0

§Values not reported.
Units for 1974 are in mg/l, while all units for 1975 and 1976 are in lbs/day.

Table 65

Summary of the Annual Levels of Toxic Pollutants Present in the Wastewater Effluent of the Shell Refinery

Paramater	1974		1975		1976	
	Average	Maximum	Average	Maximum	Average	Maximum
Oil and Grease (conc.)	2.3	7	1.2	6	1.1	2
(quant.)	§	§	20	304	19.6	60
Phenols	0.06	0.04	0.51	5.60	0.50	4.15
Sulfides	< 0.1	<0.1	< 0.1	< 0.1	<0.1	<0.1
Mercaptans	< 0.1	<0.1	§	§	§	§
Hexavalent Chromium	0.005	0.06	0.08	0.33	0.07	0.36

[§] Values not reported.
Units for 1974 are in mg/1, while all units for 1975 and 1976 are in lbs/day.

Table 66

Summary of Annual Levels of Toxic Pollutants Present in the Wastewater Effluent of the Texaco Refinery

Parameter	1974		1975		1976	
	Average	Maximum	Average	Maximum	Average	Maximum
Oil and Grease (conc.)	4.8	15	216	12	2.8	10
(quant.)	§	§	66	496†	70	238
Phenols	0.12	2.0	1.6	10.8†	1.5	35.0†
Sulfides	<0.1	<0.1	0.4	5.1	0.4	5.2†
Mercaptans	<0.1	0.5	§	§	§	§
Hexavalent Chromium	<0.1	0.2	0.1	1.9	<0.1	1.3†

[§] Values not reported

[†] Exceeded NPDES permit levels.

Units for 1974 are in mg/l, while all units for 1975 and 1976 are in lbs/day.

Table 67

Summary of Annual Levels of Toxic Pollutants Present in the Wastewater Effluent of the U.S. Oil & Refining Refinery

Parameter	1974		1975		1976	
	Average	Maximum	Average	Maximum	Average	Maximum
Oil and Grease (conc.)	13.1	38.8	13.9	39.7†	13.8†	38.6†
(quant.)	§	§	§	§	§	§
Phenols	0.64	1.73	0.27	1.13	0.31	1.35†
Sulfides	<0.1	0.1	0.11	0.18	0.14	0.16
Mercaptans	§	§	§	§	§	§
Hexavalent Chromium	§	§	<0.015	<0.015	0.013	0.015

§Values not reported

†Exceeded NPDES permit levels.

Units for 1974 and 1975 are in mg/l, while all units for 1976 are in lbs/day.

Table 68

Summary of Annual Levels of Toxic Pollutants Present in the Wastewater Effluent of the Sound Refining Refinery

Parameter	1974		1975		1976	
	Average	Maximum	Average	Maximum	Average	Maximum
Oil and Grease (conc.)	5.5	11.8	6.1	32.6[†]	3.9	12.0
(quant.)	§	§	§	§	§	§
Phenols	0.35	0.86	0.41	1.2[†]	0.26	0.92
Sulfides	0.2	0.5	0.3	1.4[†]	0.2	0.6
Mercaptans	§	§	§	§	§	§
Hexavalent Chromium	§	§	§	§	§	§

[§] Values not reported

[†] Exceeded NPDES permit levels.

All units are in mg/l.

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